INVESTIGATION OF ACTIVATED CARBON AS ADSORBENT FOR PAINT INDUSTRY WASTEWATER TREATMENT

By

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DECLARATION

I hereby declare that this thesis entitled "**Investigation of Activated Carbon as Adsorbent for Paint Industry Wastewater Treatment"** was composed by myself, with the guidance of my advisor, that the work contained herein is my own except where explicitly stated otherwise in the text, and that this work has not been submitted, in whole or in part, for any other degree or processional qualification.

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CERTIFICATE

This is to certify that the thesis prepared by **Mr. Takele Sime** entitled "**Investigation of Activated Carbon as Adsorbent for Paint Industry Wastewater Treatment"** and submitted in fulfillment of the requirements for the Degree of Master of Science complies with the regulations of the University and meets the accepted standards with respect to originality and quality

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ABSTRACT

Paint industry is one of the industries that cause water pollution by generating wastewater primarily from cleaning operations of mixers, reactors, blenders, packing machines and floors. This study aimed to evaluate the activated carbon prepared from canna indica Linn stem for the treatment of paint industry wastewater. Canna indica activated carbon was prepared by chemical activation agent using H_3PO_4. The activated carbon was characterized using physico-chemical properties such as moisture content, ash content, volatile matter content, fixed carbon content and iodine number. Totals of 6 wastewater samples were collected from Nefas Silk Paint factory wastewater using composite sampling method. The wastewater samples were physico-chemically characterized before and after treatment according to standard procedure using activated carbon as adsorbent. The required working solution was prepared using analytical reagent grade 99.8% lead nitrate. Batch adsorption studies were conducted to evaluate the optimum condition for the removal of Pb (II) from synthetic wastewater and the effects of pH, adsorbent dose and the initial concentration of were studied. The adsorptions isotherms were determined by correlation with Langmuir and Freundlich isotherms models. The results showed that the physico-chemical characteristic of activated carbon were 5.43% moisture, 5.00% ash, 26.67% Volatile matter, 62.90% fixed carbon, 40.00% yield, 1.51g/cm^3 specific gravity, 0.44g/cm^3 bulky density, 93.00% porosity and 797.48mg/g iodine number. The initial paint wastewater characteristic results were 2.95 Pb (II), 1.95 Cu (II), 171.00 BOD_5, 2401.70 COD, 619 TSS, 557.00 TDS mg/L and turbidity 2791.33 NUT. Batch adsorption was conducted to evaluate optimum condition which were (pH 5, adsorbent dose 1.5gm and initial concentration 70 mg/L) Pb (II) removal efficiency 97% for synthetic wastewater and 85.3 % for real wastewater at its optimum condition. The removal efficiency study were also conducted for the reduction of BOD_5, COD, ,Cu (II), TSS, TDS and turbidity value which were (85.30%, 93.77%, 91.30%, 77.70%, 64.40% and 99.6%) respectively. The Langmuir isotherm model provides the best correlation of (R^2) was 0.988. Finally the finding conclude that, the activated carbon produced from canna indica Linn stem has a good capability in removal of pollutants in paint industry wastewater.

Keywords: Removal Pb (II), Canna Indica Linn, Activated Carbon, Optimal Conditions

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LIST OF ABBREVIATIONS AND ACRONYMS

AC	Activated Carbon
ANNOVA	Analysis of Variance
AOAC	Association of Official Analytical Chemist
APAES	Microwave Plasma Atomic Emission Spectrometer
ASTM	American Standard test Method
AWWA	American Water Work Association
CILSAC	Canna Indica Linn Stem Activated Carbon
DOE	Design of Experiments
EEPA	Ethiopia Environmental Protection Authority
FTIR	Fourier Transform Infrared
GAC	Granular Activated Carbon
MC	Moisture Content
PAC	Powdered Activated Carbon
UNWWDR	United nations world water development report
USEPA	United States of Environmental Protection Agency
VC	Volatile Content
WHO	World Health Organization
X- RD	X-Ray Diffraction Spectroscopy

1. INTRODUCTION

1.1. Background

Water is a limited natural resource and fundamental for life and health (Dobriyal et al., 2014). About 97.5% of all water on earth is salt water and the remaining 2.5% is fresh water. Around 70% of fresh water is frozen in the Antarctica and Greenland icecaps. Only 1% of the earth‘s fresh water is accessible for extraction and human use (Corcoran, 2010). Water is important for life and for processing various materials in industry. Living organisms cannot exist without water, and almost all industries require water to operate. With rapid development of science and technology, industrial pollution and natural resource destruction rate is increasing, the human life gradually affected. Water pollution has become an increasingly serious issue to human survival and economic development on the world (Yong, 2017). Wastewater often contains both organic and inorganic pollutants; organic wastewater is generally used by biological treatment method and inorganic wastewater is treated by physical, chemical and physical-chemical methods (Young, 2017). Industrial wastewater is one of the major pollution sources in the pollution of water resource .During the last century a large amount of industrial wastewater was discharged in to the environment (Hanchang, 2009).

Industrial activities are seen as motor behind many of the processes usually termed “social transformation” and “modernization”. Paint industry is one of the industries that cause water pollution. Paint wastewater generally consists of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic, emulsifying agents, anti-foaming agents (Dey *et al*., 2004). The wastewater is generated primary due to cleaning operation of mixers, reactors, blenders, packing machines and floors (Aboulhassane *et al*., 2014). The untreated paint effluent contains high mounts of heavy metals, biological oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solid (TSS), total dissolved solid (TDS) and colored material (Aboulhassane et al., 2006). The release of heavy metals into the environment through industrial effluents is a major concern, worldwide and removal of such pollutants has been a great concern during last decades. Lead is particularly common heavy metal found in paint industries’s wastewater (Ozer and Pirincci, 2006).

Lead contamination of the environment is primarily due to anthropogenic activities, making it the most toxic metal in the environment. Lead readily accumulates in the humus-rich surface layer of the soils due to its complexity with organic matter and it was reported to be the least mobile heavy metal in soils under reducing and non-reducing conditions (Abdussalam and Adekola 2005). The release of industrial wastewaters to the environment causes several adverse effects. This wastewaters commonly including include Cd, Pb, Cu, Ni and Co. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants and human being (Needlemana and Bellingerc, 2001).

People are exposed to heavy metals through inhalation, water and food/ ingestion. Several methods have been developed for decontamination of industrial wastewaters. Among different heavy metal removal methods, chemical precipitation, membrane filtration (reverse osmosis and electro dialysis), electrolytic processes, adsorption and coagulation- flocculation could be mentioned. Adsorption techniques for wastewater treatment have become more popular in recent years with regard to their efficiency in the removal of pollutants, especially heavy metal ions, color, odor and organic pollution (Khosrayi and Rakhshaee; Steinhauser, 2008).

Adsorption has advantages over other methods for remediation of heavy metals from wastewater because its design is simple; it is sludge-free and low capital intensive. Activated carbon has been reported to have high and fast adsorption capacities (Sirichote *et al*., 2002). The commonly-used procedures for removing metal ions from effluents include chemical precipitation (Ahalya *et al*., 2005). Coagulation or flocculation and ion exchange are also in use for heavy metal elimination from the environment (Amuda *et al*., 2006). These techniques, which have been reported to be expensive, also have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require proper disposal. Therefore, preparation and use of environment-friendly materials for metal remediation is desirable. Since it is the first introduction to heavy metal removal, activated carbon is the most popular and widely used adsorbent in wastewater treatment applications all over the world. In this study focuses on paint wastewater treatment by using activated carbon prepared from canna indica Linn plant stem.

By optimized the effects of pH, initial concentration and adsorbent dose for the adsorption capacity of Pb (II) in aqueous solution and then to examine the performance of the activated carbon for the removal of Pb (II), Cu (II), BOD_5, COD, TSS, Turbidity and TDS from Nefas silk paint industry wastewater at optimum condition.

1.2. Statement of the problem

Paint industries wastewater contain high load of organic matter and inorganic toxic substance such as BOD_5, COD, TSS, TDS, turbidity, colored material and heavy metals (El-Shazly *et al*., 2010). These pose serious negative impacts, not only on surface water bodies and ground water, but also in aquatic ecological system and human being. The aquatic ecosystem is going to be deteriorated due to the accumulation of organic and inorganic pollutants. Even if at low concentration the trace heavy metal including Pb (II) has a significant impact on the destructing of aquatic life as well as human health through ecological food chain. It may cause developmental and neurological disorder, kidney damage several types of cancers for human being and damage the breathing system of aquatic life like fish (Sobh *et al*., 2014)

In Ethiopia most of paint industries do not properly treat the wastewater rather discharge directly to river (Biruk .T, 2011). Recently there are more paint industries in Ethiopia which is affecting the environment and make the public risk due to the release of untreated waste (Dessalew. B and Yonas. S, 2017). Nefas silk paint factory is one of the paint industries in Ethiopia. The factory produces maximum of 87000 liters of paint per day and discharges its 2000 liters waste directly on the drainage without treating (Ribka.B, 2017). These effluents highly concentrated with organic and inorganic toxic chemicals that affect the groundwater and the surface water due the discharge of untreated effluents. The presence of heavy metal especial lead in water and wastewater is hazardous to the environment and also it is not biodegradable and tends to bio-accumulate in living organisms causing serious disease and disorder (Wang *et al* 2007). Mony process for the removal of toxic pollutants from water and wastewater haven been proposed. Chemical precipitation, physical treatment such electrochemical reduction, ion-exchange, and membrane-separation are some of the processes that have been reported to be the most effective ones in the removal of heavy toxic pollutants (Mona *et al.*, 2014). However, these processes involve use of chemicals and synthetic polymers whose impact

on the environment (Shuguang *et al.,* 2008). adsorption appears to be an attractive process due to its simplicity and cost effective for the removal of pollutant from wastewater (Malakootian *et al*., 2009). Low-cost activated carbon can be prepared from different agricultural crop and industrial wastes (Agbozu and Emoruwa, 2014). In these cases canna indica Linn plant is one of agricultural crop it can be grown in tropical and subtropical area. Canna indica Linn plant found in Ethiopia everywhere especially in south region, Amara region, Oromiya region and Addis Ababa city. It was used for homes and public parks for its decorative purpose after that disposed on open area or burnt open air, which was caused additional environmental problem. Taking this fact in to account this study was concerned with evaluation of the removals of pollutant from Nefas Silk paint industry wastewater using activated carbon prepared from canna indica Linn plant stems.

1.3. Objective of the study

1.3.1. General objective

The general objective of this study is to investigate the effectiveness of canna indica Linn stem activated carbon as adsorbent for the treatment of paint industry wastewater.

1.3.2. Specific objectives

The specific objectives of this study;

- To prepare and characterize the physico-chemical properties of canna indica Linn stem based activated carbon.
- To characterize the Nefas silk paint industry wastewater.
- To optimize pH, initial concentration and adsorbent dosage for the removal of Pb (II) from aqueous solution using the activated carbon.
- To examine the performance of the activated carbon for the removal of Pb (II), Cu (II), BOD_5, COD, TSS, Turbidity and TDS from paint industry wastewater at optimum condition

1.4. Scope of the study

This study focus on adsorption capacity of canna indica Linn plant stem based activated carbon as adsorbent for removal pollutant load from Nefas silk paint industry wastewater by optimizing the process of Pb (II) removal efficiency in aqueous solution then to evaluate the removal efficiency of Pb (II) and another competitive pollutants like Cu (II), BOD_5, COD, TSS, TDS and turbidity at the optimum condition from Nefas silk pain industry wastewater.

1.5. Significance of the study

A major challenge of many industries is finding solutions that equate to positive environmental and economic impacts regarding the treatment of their effluents (Debela .T**,** 2016). Paint industries wastewater containing organic and inorganic pollutants. These pollutants are directly or indirectly discharged into the environment, causing serious environmental pollution and even threatening human life (Yong, 2008). Conventional methods for pollutant removal from paint wastewater are often costly and have inadequate efficiencies at low metal concentrations. This research tended to solve this problem by evaluating the use of canna indica Linn plant stem based activated carbon as an adsorbent and to improve the quality of water contaminated with organic matter and inorganic toxic chemicals and helps to avoid any conflict with the surrounding communities and the authority that may arise due to the discharge limits. In addition, adsorption process by canna indica Linn plant stem activated carbon is used to helps the development of new and cheaper adsorbent material for the removal of organic matter and inorganic toxic chemicals from paint wastewater.

2. LITERATURE REVIEW

2.1. Paint

Paint is a mixture of pigment, binder, solvent and additives (Kobahti and Tonyolac, 2009). Pigment**:** Pigments are a solid material substance that dispersed thought out the paint in to color, toughness, texture or simply to reduce the cost of the paint. Although, some paints contain dyes replacements of pigments. Pigments can be categorized as synthetics or natural types. Synthetics types of pigments include calcined clays, blank fix, precipitated calcium carbonate and synthetic silica and Natural Types of pigments; various clays, calcium carbonate, mica and silica, Binder**:** binder is the main constituents of paints, binders are polymers (resins) forming a continuous film on the surface. A binder is a good adhesion, binds the pigments together, and strongly influences such properties as gloss potential, exterior durability, flexibility and toughness. Solvent:-The main purposes of the solvent are to adjust the curing properties and viscosity of the paint.

Additives: additives are other important components of paint, which are usually added in very small amounts and give a very significant effect on the product. Some important examples of additives are: modify surface tension, improve flow properties, improve the finished appearance, increase wet edge, improve pigment stability, control foaming, control skinning, and etc. common type of additives are cobalt octet, lead octets, barium and calcium octet.

Table 1: Percentage Composition of Paint

Composition	Percentage
Pigment	25%
Solvent	40%
Additive	5%
Binder	30%

Sources: (H. Asilian, 1998)

2.1.1. Paint Manufacturing Process

In general paint is produced by mixing chemicals (primarily resins, dry pigment, and pigment extenders) in a container equipped with a high-speed mixer. Solvents and drying oils also are added during this step. After mixing, the batch may be transferred to a mill for additional grinding and mixing. Then the paint base is transferred in to the color matching tank (usually a volatile naphtha or blend of solvents) and the balance of the resin are added and mixed. Upon reaching the proper consistency, the paint is filtered to remove any non-dispersed pigment and transferred to a loading hopper. From the hopper, the paint is poured into cans, labelled, packed, and stored in the proper place.

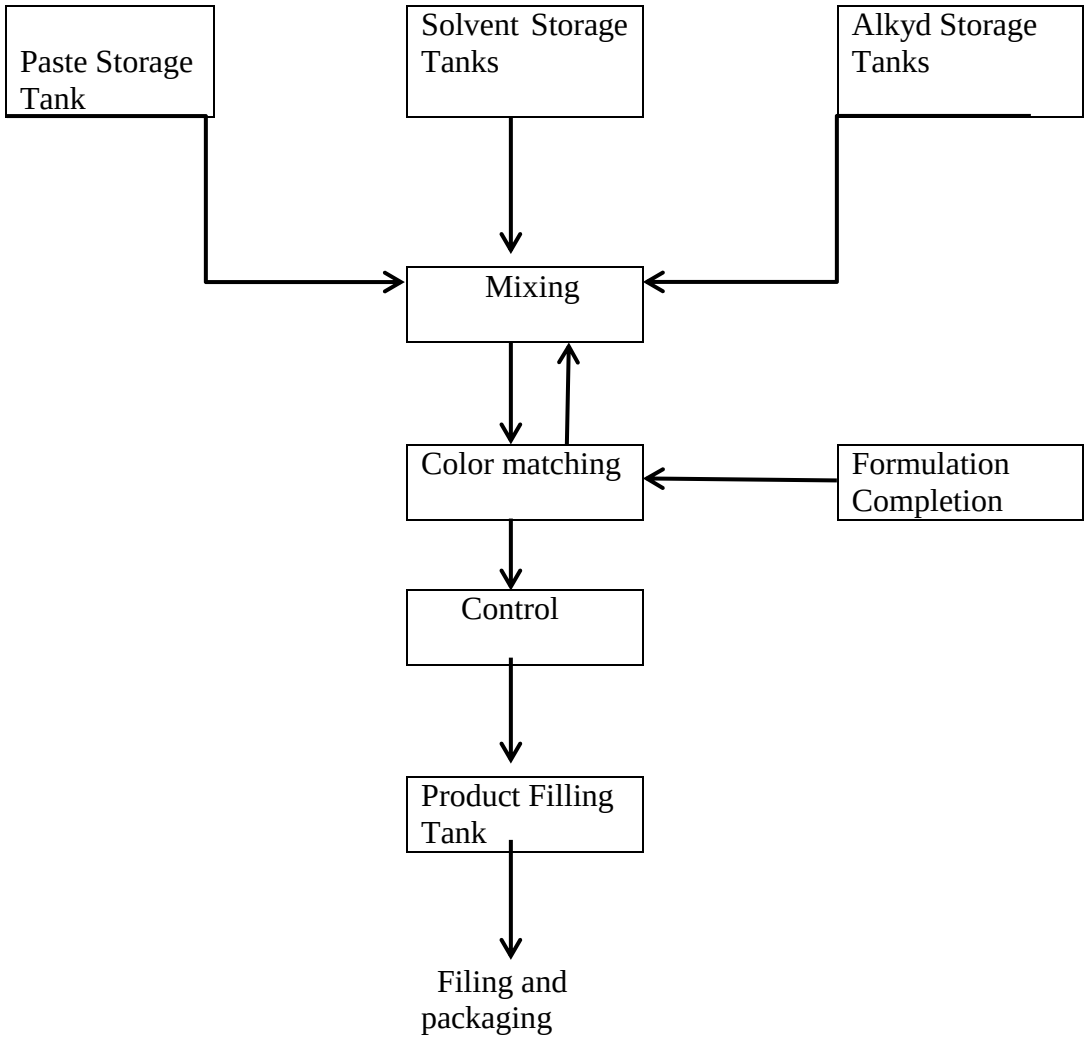

Figure 1: General Diagram of Paint Production Process (Dursun and Sengul, 2006)

2.2. The Characteristics of Paint Industries Wastewater

Paint wastewater is characterized by high toxic and high concentration of organic pollutants (Korbahti and Tanyolac, 2009). It is highly contaminated with heavy metal, biological oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended (TSS), total dissolved solid (TDS), Phosphorous (P) and color materials (Tariq *et al*, 2006). The sources of paint industries wastewater is generated primary due to cleaning operation of mixers, reactors, blenders, packing machines and floors with the varying degree of chemical used (Li *et al*., 2018)

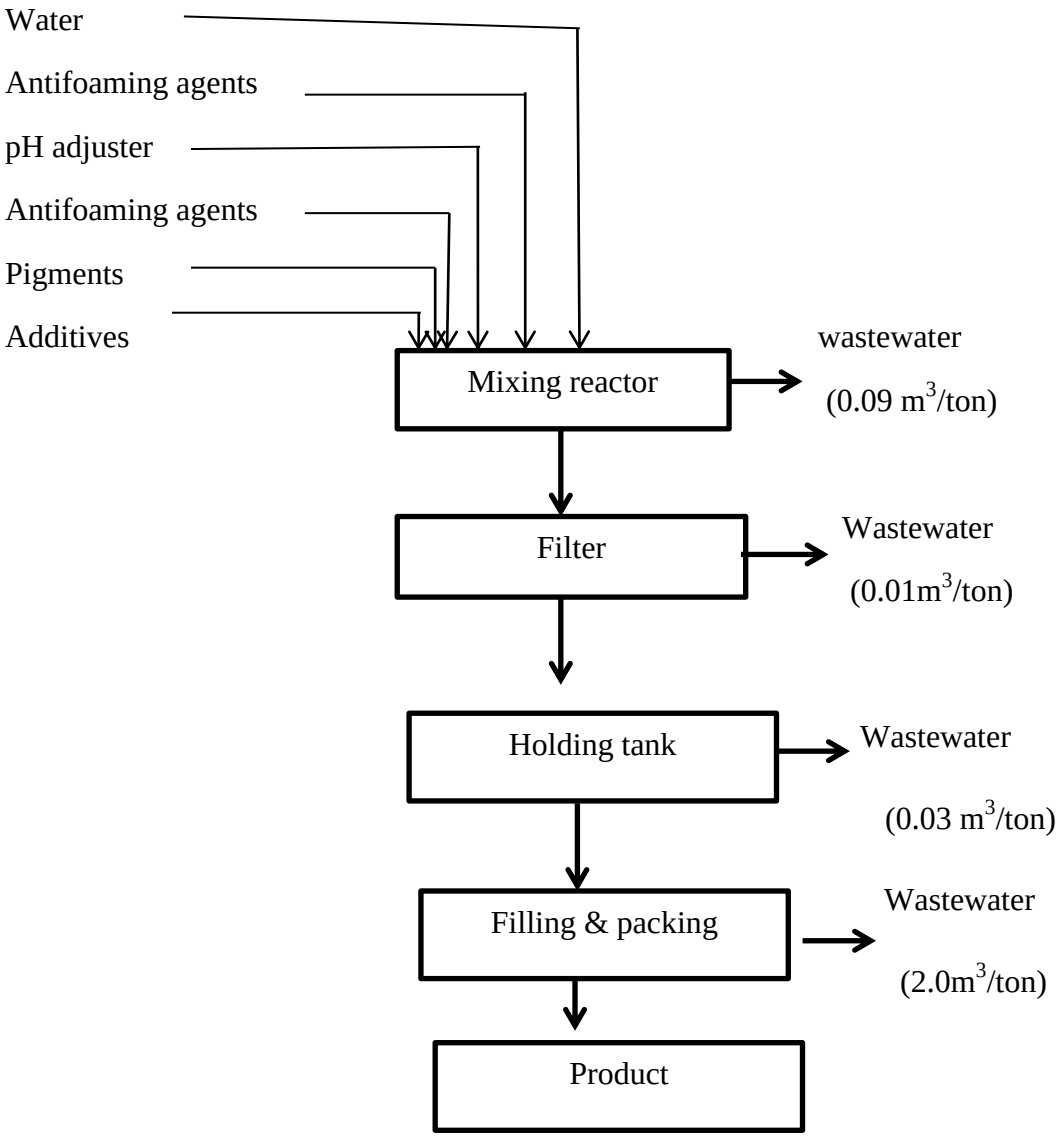

Figure 2: Source of Wastewater In Paint Industries (Kutluay *et al*., 2004)

2.2.1. Environmental Impacts of Paint Wastewater

The discharge of paint industrial effluents through drains and canals to rivers deteriorate and increase water pollution. The High levels of pollutants in river water causes an increase in biological oxygen demand (BOD_5),chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), toxic metals such as Cd, Cr, Ni and Pb and fecal coliform and hence make such water unsuitable for drinking, irrigation and aquatic life (Aydin and Balik, 2016). Wastewater from paint industry has the highest amount of heavy metals concentrate them most hazardous for soil, plant and other organisms including human being. These industrial effluents with heavy metals could be toxic and accumulated in the receiving environment, causing adverse effects on indigenous biota (Chukwujike *et al*., 2015).

2.2.2. Impacts of Organic Pollutants

When a biodegradable organic waste is discharged into an aquatic ecosystem such as a lake, stream or rivers, oxygen dissolved in the water is consumed due to the respiration of microorganisms that oxidise the organic matter. The more biodegradable a waste is, the more rapid is the rate of its oxidation and the corresponding consumption of oxygen. Because of this relationship and its significance to water quality (dissolved oxygen levels in the water), the organic content of wastewaters is usually measured in terms of the amount of oxygen consumed during its oxidation, termed the Biochemical Oxygen Demand (BOD).In an aquatic ecosystem, a greater number of species of organisms are supported when the dissolved oxygen (DO) concentration is high. Oxygen depletion due to waste discharge has the effect of increasing the numbers of decomposer organisms at the expense of others. When oxygen demand of a waste is so high as to eliminate all or most of the dissolved oxygen from a stretch of a water body, organic matter degradation occurs through the activities of anaerobic organisms, which do not require oxygen (Meertens *et al*., 2000). Not only does the water then become devoid of aerobic organisms, but anaerobic decomposition also results in the formation of a variety of foul smelling volatile organic acids and gases such as hydrogen sulphide, methane and mercaptans (certain organic sulphur compounds).

The stench from these can be quite unpleasant and is frequently the main cause of complaints from residents in the vicinity. Chemical Oxygen Demand (COD) is the measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. It does not differentiate between biologically available and inert organic matter. COD values are always greater than BOD values, but COD measurements can be made in a few hours while BOD measurements usually take five days (BOD). Turbid waters are also not usually good for living things in the water. Because less light can go through the water, it's not good for plants growing in the water. Fine suspended solids can bury animals in the stream bottom and cause problems for fish. Toxin producing algae can kill of wildlife, are dangerous for people who eat fish in these areas, and can eventually kill nearly everything in the water when they die and consume all the oxygen in the water.

2.2.3. Impacts of Heavy Metals

Heavy metal pollution is one of the major environmental concerns today because of their toxicity, threat to human life and the environment. They can accumulate in living tissues causing various diseases and disorders (Okafor *et al*., 2015). Many industrial processes, such as mining, refining ores, fertilizer industries, tanneries, photography, surface finishing, energy and fuel producing, steel, battery manufacturing, paper industries, paint industries etc, result in the release of heavy metals to aquatic ecosystems (Buasri *et al*., 2012). Their presence in receiving lakes and streams could lead to bioaccumulation in living organisms leading to several health problems such as cancer, reduced mental and central nervous function (Eneji et al., 2013). The composition of heavy metals from industrial wastewater is a major concern for the environment, based on the rich of copper (Cu), lead (Pb), chromium (Cr) and cadmium (Cd), (Zwain *et al*., 2014). The removal of these metals by sorption from rivers and wastewaters is important in order protect public health and the balance in ecosystems.

2.2.3.1. Impacts of Lead

Pb (II) ions is one of the major pollutant in paint industry wastewater and it's has a high toxicity and tendency to accumulate in tissues of living organisms (Mubaraka *et al*., 2012). Pb can occur in different forms such as organic and inorganic forms. Pb (II) is the most significant toxin of the trace metal ions, and human exposure to the inorganic forms is through ingestion of food, water, and inhalation. Pb (II) affects mainly the peripheral nervous system and haematopoietic, renal, gastrointestinal, cardiovascular, and reproductive systems. Organic Pb (II) mainly affects the central nervous system. According to (WHO, 2014), the permissible level for Pb (II) in drinking water is 0.05 mg/L. Therefore, it is necessary to remove Pb (II) from wastewaters before discharging into the natural water bodies.

2.3. Environmental Principles, Policy and Standards in Ethiopia

2.3.1. Environmental Principles in Ethiopia

Pollution is a growing urban environmental challenge in Ethiopia. Developmental activities that likely cause pollution or other environmental hazard shall have an obligation to install sound technologies or adopt practices that minimize or avoid the generation of waste and to promote the reuse of waste. EPA or regional environmental agencies are empowered to require any person causing pollution to clean up or pay the cost of cleaning, and to prevent any harm including closure or relocation of operation that cause imminent danger to health and environment. This in line with the polluter pay principle is accepted as one of the environmental principle in Ethiopia (EEPA, 1997 and Grima, 2000).

2.3.2. Environmental Policy and Standards

Draft pollution control legislation, Article 7 provides, formulation of environmental standards regarding discharge limit of effluent to water bodies and sewage system, air quality, specifying the allowable degree of emission both for stationary and mobile air pollution sources, soil quality, and noise and waste management is the responsibility of EPA in collaboration with other agencies. EPA may prescribe different environmental standards for different area of the country as necessary to rehabilitate or protect the

environment. Based on their specific situation, national regional state may adopt environmental standard that are not strict as the federal ones.

2.3.3. Standards of Paint Effluent Discharge

Paint effluent contain high amount of heavy metals and organic pollutants so the removal of these toxic pollutants from effluent before discharging to the environment and from raw water before public use is essential for protection of human health and environment (Chukwujike *et al*., 2015). However in the wake of recent industrialization and fast urbanization the quality of groundwater has become an increasing concern due to contamination by various toxic chemicals (Chukwujike *et al*., 2015). Therefore standard is developed by the national environmental protection authority and world health organization according the local condition and environmental requirement is essential for each country Table 2 below presents the standards of paint effluent discharge from WHO (2015), US-EPA (2006) and EEPA (2003).

Table 2: The Maximum Contaminated Level (MCL) Standards, for Paint Effluent Discharge

Parameter	Unit	WHO(2015)	US-EPA (2006)	EEPA (2003)
pH	-	6.5-8.5	6 – 8.5	6-9
Temperature	^{o}c	-	-	40
Turbidity	NUT	5	15	25
DO	mg/L	30	-	5-20
BOD_5 mg/L	mg/L	15	23	50
COD (mg/L)	mg/L	40	120	150
Total suspended solid	mg/L	30	50	50
Total dissolved solid	mg/L	50	40	-
Pb	mg/L	0.04	0.05	0.5
Cu	mg/L	1	1	1

2.4. Advanced Wastewater Treatment

Advanced wastewater treatment is defined as: any process designed to produce an effluent of higher quality than normally attained by secondary treatment processes. Advanced wastewater treatment used for additional organic and suspended solids removal, removal of nitrogenous oxygen demand, nutrient removal, removal of toxic materials (Dhokpande *et al*., 2014). The most common methods for removal of pollutant from industrial effluents including: ion exchange, chemical precipitation, Electro-chemical, Membrane filtration process, flocculation and flocculation and adsorption etc.

2.4.1. Chemical Precipitation

Chemical precipitation is one of the most widely used for heavy metal removal from inorganic effluent in industry due to its simple operation (Ku and Jung, 2001). Lime and lime stone are the most commonly employed precipitant agents due to their availability and low-cost most countries (Mirbagheri and Hosseini, 2005). Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and suitable and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. The drawbacks these methods is excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Aziz *et al*., 2008).

2.4.2. Coagulation and Flocculation

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation (Hung et al., 2016). To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules (Ayoub and Semerjian, 2003). The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles.In general, coagulation–flocculation can treat inorganic effluent with a metal concentration of less than 100 mg/L or higher than 1000 mg/L the heavy

metal removal by the coagulation–flocculation process. The major advantages of coagulation and flocculation methods are improved sludge settling, dewatering characteristics, bacterial inactivation capability, sludge stability are the most common property of coagulation and flocculation. The major drawback of coagulation–flocculation method is it is high operational cost due to chemical consumption. The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment. This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment (Ayoub *et al*., 2001).

2.4.3. Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal.

Ultrafiltration (UF): Ultrafiltration utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000– 100,000 Da). These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (Vigneswaran *et al*., 2004). UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density. However, the decrease in UF performance due to membrane fouling has hindered it from a wider application in wastewater treatment. Fouling has many adverse effects on the membrane system such as flux decline, an increase in transmembrane pressure (TMP) and the biodegradation of the membrane materials (Kurniawan *et al*., 2006).

Nanofiltration (NF): Nanofiltration has unique properties between UF and RO membranes. Its separation mechanism involves sieving and electrical effects. Potential is created between the charged anions in the NF membrane and the co-ions in the effluent to reject the latter (Van der Bruggen and Vandecasteele, 2003). The significance of this membrane lies in its small pore and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts. In general, NF membrane can treat inorganic effluent with a metal concentration of 2000 mg/L. Depending on the membrane characteristics, NF can effectively remove metal at a wide pH range of 3–8 and at pressure of 3–4 bar. The limitation of nanofiltration method is that it is Costly and prone to membrane fouling.

Reverse osmosis (RO): In reverse osmosis (RO), a pressure-driven membrane process, water can pass through the membrane, while the heavy metal is retained. Unlike chemical precipitation, instead of pH, pressure is the major parameter that affects the extent of heavy metal removal by RO. The higher the pressure, the higher the metal removal efficiencies, and thus the higher the energy consumption. The other advantages of using RO include a high water flux rate, high salt rejection, resistance to biological attack, mechanical strength, chemical stability and the ability to withstand high temperatures. The reuse of water from industrial process can be achieved and RO enables industrial users to comply with the effluent limit of the discharge standards imposed under environmental legislation. In spite of its benefits, RO has some limitations. Due to the suspended solids or oxidized compounds such as chlorine oxides, the small pores of the membrane make it more prone to fouling (Potts et al., 2000). The cations such as Cd (II) and Cu (II) present in the contaminated wastewater promote membrane fouling, which might be irreversible. The membrane would then have to be replaced, thus increasing the operational costs. Membrane performance also decreases over time, resulting in the decreasing permeate flow rate (Ning, 2002). Other major drawbacks are the high energy consumption, the scaling of $CaCO_3$ or $CaSO_4$ and the need for experienced personnel to run the process (Ayoub and Malaeb, 2011).

2.4.4. Electrochemical methods

Electro chemical method is one of technology used to remove metals from wastewater streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Various types of electro chemical method such as electro-Dialysis (ED), Membrane electrolysis (ME) and electrochemical precipitation (EP).

Electro-Dialysis (ED): Electrodialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation- exchange membranes (Chen. 2004). The main disadvantages Electrodialysis (ED) are its requires higher energy and its require higher operation cost (Kurniawan et al., 2006).

Membrane electrolysis *(*ME*):* Membrane electrolysis, a chemical process driven by an electrolytic potential, can also be applied to remove metallic impurities from metal finishing wastewater. There are two types of cathodes used: a conventional metal cathode (electrowinning) and a high surface area cathode (Janssen and Koene, 2002). When the applied electrical potential across an ion exchange membrane, reduction–oxidation reaction takes place in electrodes (Acheampong, 2013). Unlike Electro-Dialysis (ED). Membrane electrolysis can be employed to treat plating wastewater with a metal concentration of higher than 2000 mg/L or less than10 mg/L. The major drawback of membrane electrolysis (ME) is its high energy consumption (Khatoon, et al., 2016).

Electrochemical precipitation (EP): To maximize the removal of heavy metal from contaminated wastewater, electrical potential has been utilized to modify the conventional chemical precipitation. Electrode stabilization of colloids is called coagulation and precipitation by hydroxide formation to acceptable levels. It is the most common heavy metal precipitation method forming coagulants by electrolytic oxidation and destabilizing contaminants to form folc (Mollah, et.al, 2001). The electro-coagulation process the coagulant is generated in situ by electrolytic oxidation of an appropriate

anode material. In this process, charged ionic metal species are removed from wastewater by allowing it to react with anion in the effluent. In general, electrochemical precipitation processes can treat inorganic effluent with a metal concentration higher than 2000 mg/L. The major drawback of electrochemical chemical precipitation (EP) are huge sludge production, slow metal precipitation, poor settling, the aggregation of metal precipitates and the long-term environmental impacts of sludge disposal (Aziz, *et.al*, 2008).

2.4.5. Ion Exchange

Ion exchange is also one of the most frequently applied treatments worldwide for wastewater laden with heavy metals. In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin (Vigneswaran et al., 2004) Ion exchange can also be used to recover valuable heavy metals from inorganic effluent (Dąbrowski, 2004). After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents. The disadvantage of this method is that it is .not all ion exchange resin is suitable for metal removal and high capital cost (Nguyen et al., 2011). Therefore, the use of other method such as adsorption, adsorption appears to be an attractive process due to its simplicity, effectiveness and economical in the removal of pollutant from wastewater.

2.5. Adsorption

Adsorption is a widely used method for the treatment of industrial wastewater having color, heavy metals and other inorganic and organic impurities. The benefits of adsorption process are for its simplicity in operation, inexpensive (compared to other separation processes and without sludge formation (Mojiri *et al*., 2014). Adsorption refers to the attachment of substances from a liquid or gaseous phase to solids. The solid is referred to as the adsorbent. The substance taken up is called the adsorbate. Adsorption has important for industries which use for removal of metal from industrial wastewater. Removal of dyes from industrial wastewater, Recovery of dyes from dilute solution, gas masks containing adsorbents to purify the air from poisonous gases and vapors, removal of impurities from petroleum oils, Inactivation of bacteria toxin, hormone or a mineral or

as antidote in cast of poisoning, removal of impurities from motor spirits, purification of enzymes, clarification of sugar liquid, separation of gas mixture, in chromatographic analysis, In softening of hard water, in drying gases, decolourisation and purification (Halnor, 2015).

Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. The attachment of atoms or molecules of adsorbate on the surface of solids and liquids may be through two types of forces, physical or chemical. Depending upon the types of forces involved in adsorption (Halnor, 2015) it may be divided into two types, physical adsorption or physisorption and chemical adsorption or chemisorptions. Physical adsorption**: -** this phenomenon involves the use of weak Van der Waal forces by means of which gas molecules get adsorbed on a solid surface. Chemical adsorption**: -** In chemical adsorption when the forces of attraction between the adsorbate and the adsorbent are chemical bonds.

Adsorption mechanism

The classical mechanisms of adsorption is divide into three stages (Fig.2.3): a) diffusion of adsorbate to adsorbent surface, b) migration into pores of adsorbent c) monolayer build-up of adsorbate on the adsorbent

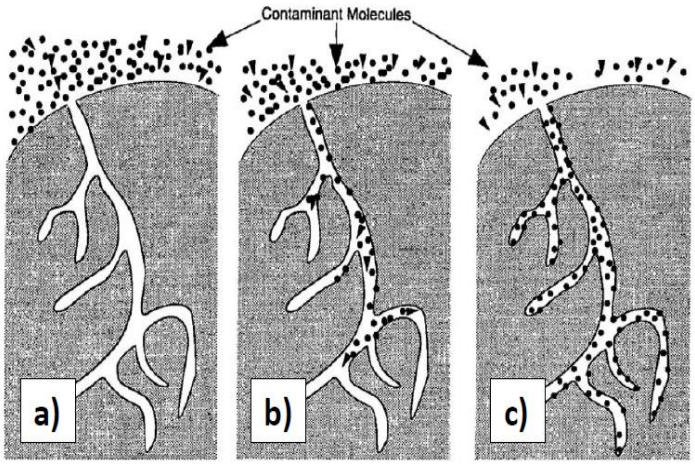

Figure 3: Three Steps of Adsorption Mechanisms**.**

From figure 3 presented the process of adsorbate distribution. Stage1 occurs diffusion of adsorbate on the adsorbent surface by intermolecular forces between adsorbate and adsorbent. The second step involves migration of adsorb ate into pores of adsorbent. During the last step, when the adsorbate' s particles are distributed on the surface and filled up the volume of pores, particles of adsorbate are building up the monolayer of reacted molecules, ions and atoms to the active sites of adsorbent (Iakovleva, 2013).

2.5.1. Factor Affecting Adsorption Process

Adsorption is one of the top wastewater treatment methods in the globe (Chaturvedi and Sahu, 2014). During the adsorption process the sewage is free from inorganic and organic elements like heavy metal effluents (Fomina et al., 2014).The adsorption process generally depends on the following:

2.5.1.1. The solution of pH

The pH of the solution was clearly an important parameter that controlled the adsorption process (Gupta and Rastogi, 2007).The effect of pH in turn depends on the charge on the adsorbent surface, the degree of ionization also the species of adsorbate. In a particular pH, most metal sorption is enhanced with pH, increasing in to certain value followed by a reduction when further pH increases. As it is known, change in the pH value could cause a change in the adsorption capacity (tulu and biligin, 2015).

2.5.1.2. Adsorbent Dose

The adsorbent dosage is an important parameter because this determines the capacity of an adsorbent. The removal of metal ions increases with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption was studied by varying the amount of adsorbents and keeping the other parameters constant (Azmier *et al*., 2011). Due to their relationship, adsorbent particle size is important to the process of adsorption. For example, when the number of particles size is small, the adsorption capacity increases and surface area of adsorbents increases. Particle size increases with adsorption decrease, although the surface area decreases also the adsorption capacity is inversely proportional to the size of the adsorbent particle on the other hand, the adsorbate surface area is directly proportional to the adsorption capacity (Moham et al., 2009). Similarly, the

surface area of adsorbents has great importance for the adsorption process due to physicochemical properties (Mohan *et al*., 2014)

2.5.1.3. Contact Time

The removal efficiency increased with an increase in contact time before equilibrium is reached. The amount adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under the operating conditions Mohammad *et al*., 2011)

2.5.1.4. Initial Metal Concentration

The initial metal ion concentration is an important driving force overcomes all mass transfer resistances of metal ion between aqueous and solid phases (Mohammad *et a*l., 2011).initial concentration of metal ions can alter the removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions (Ben *et a*l., 2017).

2.5.1.5. Effects of Temperature

Adsorption involves specific relations between the properties of activated carbon and the solute. Therefore, the quantitative effects of temperature are not the same with all carbons and solutes (Deng *et al.,* 2010). The extent of adsorption should increase with decreasing temperature because the adsorption reactions are exothermic. However, increased temperature also increases the rate of diffusion of the solute through the liquid to the adsorption sites, which eventually leads to an increased adsorption. An important difference in the adsorption of solutes versus gases is found in the role of temperature. An increase in temperature increases the tendency of a gas to escape from the interface and thus diminishes adsorption. However, in adsorption from the liquid, the influence of temperature on solvent affinities is more dominant (Gad and Omar, 2013).

2. 5.1.6. Effects of mixing rate

The mixing rate enhances the adsorption of metal ion in the solution by minimizing the mass transfer resistance and affecting the physical structure of the adsorbent (Fomina and Gadd, 2014). As mixing rate increased from 0 to 200, the adsorption capacity also increased. The adsorption increased due to the additional turbulence which enhances the metal ion diffusion into the surface of adsorbent (Park *et a*l., 2013).

2.5.2. Types of Adsorbent

Various types of adsorbents are divided into natural adsorbents and synthetic adsorbents

Natural adsorbent:- Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities.

Synthetic adsorben: - Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore mineral (Debela,2016).

2.5.3. Adsorbent Surface Modification Method

Surface modification of low- cost adsorbent is recognized an attractive approach for enhancement of pollutant removal. Modification can be achieved by adsorbing foreign organic compound on the surfaces of carbons. There are two methods available to modify adsorbent such as physical and chemical modification (Wigmans, 2000).

2.5.3.1. Physical Modification Method

Surface area and the pore volume of the adsorbent may be enhanced by physical modification; the most common method of physical modification is heat treatment, in which the low cost adsorbent is treated in an inert atmosphere at high temperature. The significant disadvantage of this method is the decomposition of surface oxygen base functional groups, which are thermally unstable (Wigmans, 2000).

2.5.3.2. Chemical Modification

Surface modification of the surface of the low cost adsorbent is possible through reaction with an acid and base. Based on this fact the method divide in to major categories such acid surface modification and base surface modification (Mohammed *et al*., 2010) Chemical modification using base in this method the preparation of activated carbon, the lignocellulosic precursor is treated primarily with a chemical agent, such as NaOH, KOH or ZnCl2 by impregnation or physical mixture and the resulting precursor is carbonized at temperatures between 400 and 800ºC under a controlled atmosphere. Chemical modification using acid in this method the preparation of the low cost adsorbent is treated with a chemical agent such as H_3PO_4, H_2SO_4 and HNO_3 by impregnation or physical mixture and the resulting precursor is carbonized at temperatures between 400 and 800ºC under a controlled atmosphere.

H_3PO_4 as surface modification agent for adsorbent preparation

H_3PO_4 is an important chemical agent for surface modification of the preparation of adsorbent that acts as an acid catalyst to promote bond cleavage, hydrolysis, dehydration and condensation, accompanied by cross-linking reactions between phosphoric acid and biopolymers; it also function as a template because the volume occupied by phosphoric acid in the interior of the activated precursor is equal with the micropore volume of the activated carbon obtained (Zuo *et al*., 2009). H_3P0_4 is one of widely used chemical as activation agent for lignocellulose materials. It has been used for a wide variety of cellulosic precursors such as banana stem and bagasse (Misran *et al*., 2015), coconut shells (Gratuito, 2008)), nut shells (Zhong et al., 2012), apple pulp (Hesas *et al*., 2013), peanut hull (Girgis *et al* 2002) and etc. in addition H_3PO_4 is the most preferred chemical agent because of low environmental pollution to compare Compared $Zncl_2$ (Girgis *et al*., 2002)

2.5.3.4. Activated Carbon

Activated carbon is a tasteless solid, microcrystalline, non-graphitic form of black carbonaceous material with a porous structure (sugumaran *et al*., 2012). Carbonaceous material a unique and versatile adsorbent because of it has high mechanical strength stability in physicochemical properties degree of surface reactivity, it also characterized with very large surface area up to 2000 m^3/g (Misran et al., 2017). AC is applied widely in a variety of fields such as food and chemical industries, wastewater treatment, solvent recovery, air pollution control and hydrometallurgy for the recovery of gold and silver (Misran *et al*., 2017)

2.6. Canna Plants

Canna is a genus of nineteen species of flowering plants (prince, 2010). The closest living relations to cannas are the other plant families of order zingiberales that is the gingers, banana, maranatas, heiconias, strelitzias (Kodama and Konagaya 2014). Canna is the only genus in the family cannaceae. Family has almost universally been recognized by taxonomists. The species have large, attractive foliage and horticulturists have turned it into a large-flowered and bright garden plant (Kodama and Konagaya 2014). Although a plant of the tropics, most cultivars have been developed in temperate climates and are easy to grow in most countries of the world as long as they can enjoy at least 6–8 hours average Sunlight during the summer. The life cycle of different species of Canna is of approximately 9 months. Cannas begin their life just after the end of winter. The lifecycle begins by producing leaves from the buds of underground rhizomes.

During the early days, these plants require an average temperature of 15-20°C, average relative humidity of 79%, and rainfall of 54 mm. These ornamental plants continue to grow in the above mentioned climate to reach their maximum length. Blooming begins in their adult stage and continues till late autumn. During summer, Cannas reach their maximum size with abundant fruits and seeds. Germination of seeds rarely occurs because of the hard seed coat. The aerial parts of Canna start drying during the summer. The dried plant remains underground throughout the winter season and again starts its life cycle in the next season.

Canna indica Linn plant is one of canna species flowering plants. Canna indica is commonly called ‘’India shot’’ and belongs to the *cannaceae* family. Canna indica is a nature of tropical and is a very popular ornamental and agricultural plant. Canna indica is robust perennial plants that grow from a think; branching, underground rhizome can be to 1-3 meter in height and from compact mass, being enclosed by covers leaves. The leaves are large green or purplish green with short petioles and elliptic plates can measure from 30 to 60 cm long and 10 to 25cm wide, with wide base and narrowing at the wedge and the apex is short sharp and acute. Inflorescence is in terminal clusters with 6-20 groups of 1-2 flowers. The fruits are ellipsoid capsules that are globose warty, 1.5 to 3 cm in length trunk nut color, with amount of black and very hard seeds. Canna indica can be grow from sea level to 900 meters but increases in mountainous tropical and subtropical temperature climates, between 1,000 and 2000. It likes average temperature from 14 to 27^{o}Cand minimum annual rain fall of 500 mm to 1,200 mm. it grows very well in light soils (Borin *et al*., 2011).

Figure 4: Canna indica Linn plants

Canna indica Linn plant was found in Ethiopia everywhere especially in south region, Amara region, Oromiya region and Addis Ababa city. It was used for homes and public parks for its decorative purpose.

Table 3: Elemental Analysis of Canna Indica Linn Plant

Elements	%
Carbon	40.58 ± 0.27
Nitrogen	1.32 ± 0.09
Oxygen	52.49 ± 0.48
Hydrogen	5.01±0.19
Sulphur	0.26 ± 0.03
Ash	0.62 ± 0.26
Moisture	9.24 ± 0.43
Lignin	5.36 ± 0.30
Cellulose	31.30 ± 0.27
Hemicellulose	31.05 ± 0.93

Sources: (Borin *et a*l., 2011)

2.7. Adsorption Model

Adsorption isotherms display the dependence of the amount of adsorbed substance from the solution concentration at constant temperature. The adsorption capacity of adsorbent is determined by using the adsorption isotherm models. The most commonly used isotherms for modeling adsorption processes in liquid phase are the Freundlich and Langmuir isotherm models (Willis, 2009 and Repo, 2011). Adsorption isotherms help to design experimental system and to evaluate it, based on isotherm models, such as Freundlich and Langmuir isotherm models, and to find out a deviation between experimental data and isotherm models. Adsorption isotherms are helping to describe surface processes of adsorbent, type of adsorbate monolayer or mul-tilayer and capacity of adsorbent, which were used for this work (Willis, 2009 and Repo, 2011).

2.7.1. Langmuir Isotherm Model

According to the Langmuir model, adsorption occurs uniformly on the active sides of the adsorbent. The Langmuir isotherm model is described in the following formula (Iakovleva and sharam, 2013)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L\, q_m} \quad \text{.....2.1}$$

Where qm is the maximum amount of metal ion adsorbed capacity (mg/g), qe is the amount of metal ion per unit mass of adsorbent at equilibrium (mg/g), k_L is the constant related to binding energy of adsorption, the constants in the Langmuir isotherm can be estimated by plotting of $\frac{C_e}{q_e}$ versus C_e enables the determination of isotherm constants.

Where q_m, $\frac{1}{intercet}$ and k_L, equal to intercept *.$\frac{1}{intercet}$

Adsorption equilibrium studies are important to determine the effectiveness of adsorption. In addition to this, it is also necessary to identify the adsorption mechanism.

The Important Characteristics of Langmuir Isotherm

The characteristics of Langmuir isotherm can be stated in term of dimensionless separation factor and described the type of isotherm defined by

$$R_L = \frac{1}{1 + K_L C_i} \quad \text{.....2.2}$$

Where K_L is the Langmuir constant Co is metal concentration (mg/L). The value R_L indicates the nature of the adsorption.

Table 4: RL Value for Langmuir Models

RL Value	Nature of adsorption
RL= 1	Liner
RL=0	Unfavorable
0<RL<1	Favorable
RL>1	Irreversible

2.7.2. Freundlich Isotherm Model

The Freundlich isotherm is an empirical model that is based on adsorption on a heterogeneous surface (surface with varying properties i.e. any surface properties are distributed unevenly, for example surface energy is different at certain points). This is applicable to a non ideal sorption as well as a multilayer sorption process. The Freundich model is given by the following equation(Willis, 2009 and Repo, 2011).

$q_e = k_f c e^{1/n}$ ……2.3

Where q_e is equilibrium loading in mg/ g, c_e is Equilibrium concentration in mg/L, k_f is Freundlich constant in mg/g, n_f is Freundlich exponent. The Freundlich isotherm is an empirical equation and not a physical, chemical or thermodynamic principle. Normally Freundlich isotherms are displayed in a logarithmic scale. By taking the logarithmic function of formula above the Freundlich isotherm can be represented as a linear equation.

$\log q_e = log k_f + \frac{1}{n} log c_e$ ……2.4

With an intercept of k_f and a straight lined-slope of $\frac{1}{n}$ where k_f roughly indicates the adsorption capacity, and $\frac{1}{n}$ Adsorption intensity.

The Freundlich exponent n_f has a critical influence on the profile of the adsorption isotherm. In the field of water treatment, we are usually aiming for very low equilibrium concentrations. In this case, the equilibrium concentration corresponds to the maximum permitted adsorbate concentration in the treated water. As such, in the case of Freundlich exponents < 1 we also talk about a favorable isotherm curve. Accordingly, in Freundlich exponents > 1 there is an unfavorable curve. The Freundlich exponent therefore allows us to express how well a substance can be adsorbed. Where: The smaller the Freundlich exponent, the better the adsorbate can be adsorbed.

3. MATERIALS AND METHOD

3.1. Description of Study Area

Sample of wastewater was taken from Nefas Silk paint factory, which is found in Addis Ababa the sub city of Nefas Silk Lafto. Nefas Silk Paints Factory is the oldest Paints Factory in Ethiopia. Since 1967 it has been produce paints for walls, metallic objects and woods; Varnishes, Antirusts, Board Paints, Automotive Paints, Glues, Traffic and Road Markings, Industrial Paints and others. The factory produces maximum of 87,671 liters of paint per day and as a results it generates about 2000 liters of liquid waste on average per day (Nefas Silk Paints Factory documents, 2005-2010). Untreated wastewater had been discharging into the Akaki River since its establishment. The river continues to flow into the main Aba Samuel River. Paint wastewater is one of the most complexes, troublesome and strong industrial effluent, having high chemical oxygen demand (COD), total suspended solids (TSS) and heavy metals (Malakootian et al., 2009). The high chemical oxygen demand (COD), total suspended solids (TSS) and heavy metal amount of the paint effluent typically ranged between 3,000 – 3,500 mg/L and6,000 - 6,500 mg/L and 0.1 –15.5 mg/l respectively (Nefas Silk Paints Factory documents, 2005-2010).

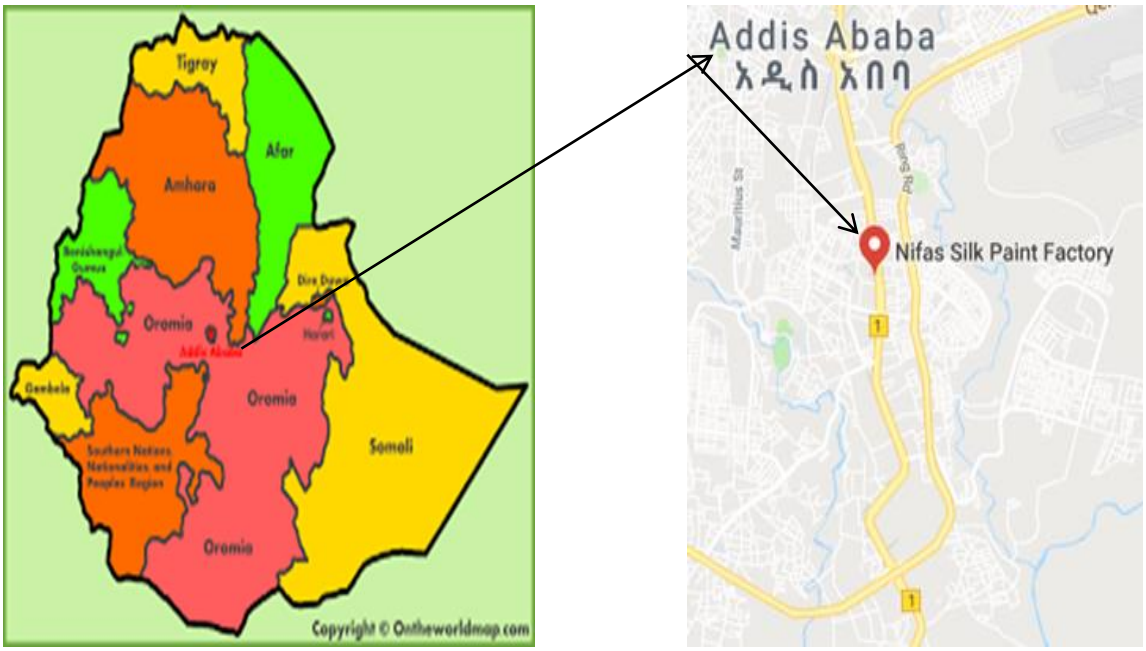

Figure 5: Location of Nefas Silk Paint Factory

3.2. Wastewater Sampling Techniques

The effluent samples were collected from "Nefas silk paint industry" found in Addis Ababa in Nefas silk Lafto sub city. The wastewater samples were collected from the equalization tank. The sampling method was done by collecting the wastewater using composite: sampling were collected two times a day as morning (9Am- 10Am) in which most of the effluent from nights work is released and afternoon (3Pm-4Pm) in which the effluent from the day times work is released and this were repeated three times in five days interval. Polythene bottle 1.5 litter was used to collectd the samples. The bottle thoroughly cleaned with hydrochloric acid, washed with tap water to render free acids, washed with distilled water twice, again cover with aluminum foil to protected sunlight during transportation period and store in refrigeration (model LR 140 S SP).

The pH, temperature and dissolved oxygen (DO) were determined immediately by using DO meter and pH meter and other parameters were analyses not immediately possible, they were preserved made by adding 1.5 ml of concentrated Nitric acid per litter of sample as stated environmental sampling and analysis for pollutants. Sampling equipment's was cleaned before sampling and at the end of sampling. All samples were mixed throughout before laboratory test to make a homogeneous.

3.2.1. Paint Wastewater Characterization and Analysis

Characterization of wastewater is very important to get exact idea about the quality of wastewater and we can compare results of different physico- chemical parameter values with standard values. The wastewater parameters analyses were selected before experimental conduct. the selected paint wastewater parameters are: The wastewater temperature, potential hydrogenation pH, dissolved oxygen, (DO), biological oxygen demand (BOD_5), chemical oxygen demand (COD), turbidity, total suspended solid (TSS), total dissolved solid (TDS), Cu (II) and Pb(II). The wastewater parameters analyses were done in the field at time of sampling, Addis Ababa sciences and Technology University in department of environmental engineering laboratory and Addis Ababa University in departments of chemistry laboratory. The water quality analyses were conducted according to the standard methods appropriate for turbid samples (AOAC, 1995).

The temperature of wastewater was measured using thermometer. pH and DO were directly measured in the field. A portable pH meter (HI 8314) HANNA calibrated with buffer standard of pH 4, 7 and 10 was used to determined pH. DO meter (OXi 3310,) WTW, calibrated automatically, and was used to determined DO. Analysis of (BOD5), COD, TSS, TDS and turbidity were carried out at Addis Ababa science and Technology University in department of environmental engineering laboratory. BOD incubator (model KBOD. 10. S) at set a constant temperature (20 ± 1°C) for five day, was used to determined (BOD5). COD was analyzed calorimetrically through the closed reflux (closed reactor) method, with potassium dichromate in sulphuric acid and silver sulphate as catalyst, by means of photometer (model DRB, 200) The Suspended solid was analyzed using filter paper (0.45 micrometer). 100 ml of sample was filtrated in the filter paper, the filter paper trapped the suspend solid then dried under 105^{o}c for 2hr then the weight of the filter paper was measured using electro balance sensitive 0.0001gm.

Then the suspended solid was calculated by using:

$$SS\ (mg/L) = \frac{B-A}{V} \quad \text{Eq.3.1}$$

Where B. is the filter paper weight before drying, A is the filter paper weight after drying, and V is the volume of the sample (100ml).

Total dissolved solid was analyzed by using sample filtration and sample evaporation method. The filtrated 50 ml of sample put the crucible in the furnace under 605^{o}c for 15 minutes then taken out the crucible and put in dyer and cooled in the room temperature. Then the total dissolved solid was calculated by using:

$$TDS\ (mg/L) = \frac{B-A}{V} \quad \text{Eq.3.2}$$

Where A is the weight of crucible, B is the weight of crucible after evaporation, V is the. Volume of sample (50ml)
Total solid was calculated by using:

$$TSS = SS + TDS \quad \text{Eq.3.3}$$

Portable turbidometer (2100a) HACH, calibrated with buffer standard turbidity 10 NUT, 20 NUT, 100 NUT and 800 NUT was used to determined turbidity. Analysis of Pb (II) and copper Cu (II) were carried out at Addis Ababa University in departments of

chemistry laboratory. Pb (II) and Cu (II) were analyzed by using Microwave Plasma Atomic Emission Spectrometry (model Agilent mp-aes 4200). The water quality analyses were done triplicated for each parameter. The removal efficiency of the activated carbon was determined as follows.

Removal efficiency = $(\frac{C_O - c_f}{c_o}) * 100$.....Eq.3.4

Where, C_o is initial parameter of concentration and c_f is the final parameter concentration

3.3. Raw Material Collection and Pretreatment

The raw material used for this study, Canna indica plant stems was collected from local canna garden area in Nolawi School which is located in Addis Ababa Akakikality sub city. Before conducting an experiment, plant species identification was conducted. Canna plant was taken off and brought to Addis Ababa University Department of Plant Biology and Biodiversity Management. The plant species was identified as scientific name of *canna indica Linn* and the family name of *Cannaceae*. All stems were taken in one place then brought to Addis Ababa Science and Technology University in departments of environmental engineering laboratory and then the Canna Indica Linn stem was dried on the sun for four day then cut into small size and washed with distilled water to remove dirt particles then dried in the oven at 105˚c for 24hr to eliminate its moisture content. The dried sample was stored in air tight plastic bags for further experiment.

3.3.1. Preparation of Activated Carbon

The methods to produce activated carbon from banana stems were conducted according to (Danish *et al*., 2018). The dry sample was grinded in to powder then one hundred grams of the Canna Indica Linn powder were mixed with 100ml concentrated phosphoric acid (85% w/w). Impregnation ratio1:1 at room temperature for 24hr then the impregnated sample was place in oven at 105^{o}C for 24hr. The dry sample was put in the dry and known weight of crucible and then the crucible was placed in rectangular furnace (model F 330). Carbonization was performed at 500^{o}C with heating rate of 25^{o}C/min. The sample was ignited in the furnace for 2hr and then removed and cooled to room temperature. The product was temporarily stored in a desiccator for some time. After that the product continuously washed with distilled water until neutral solution achieved.

After washing the product was dried in oven for 24hr and grinded using mortar then sieved in size range 125 micrometer. Finally the product was stored in air tight plastic bags till used in adsorption experiment.

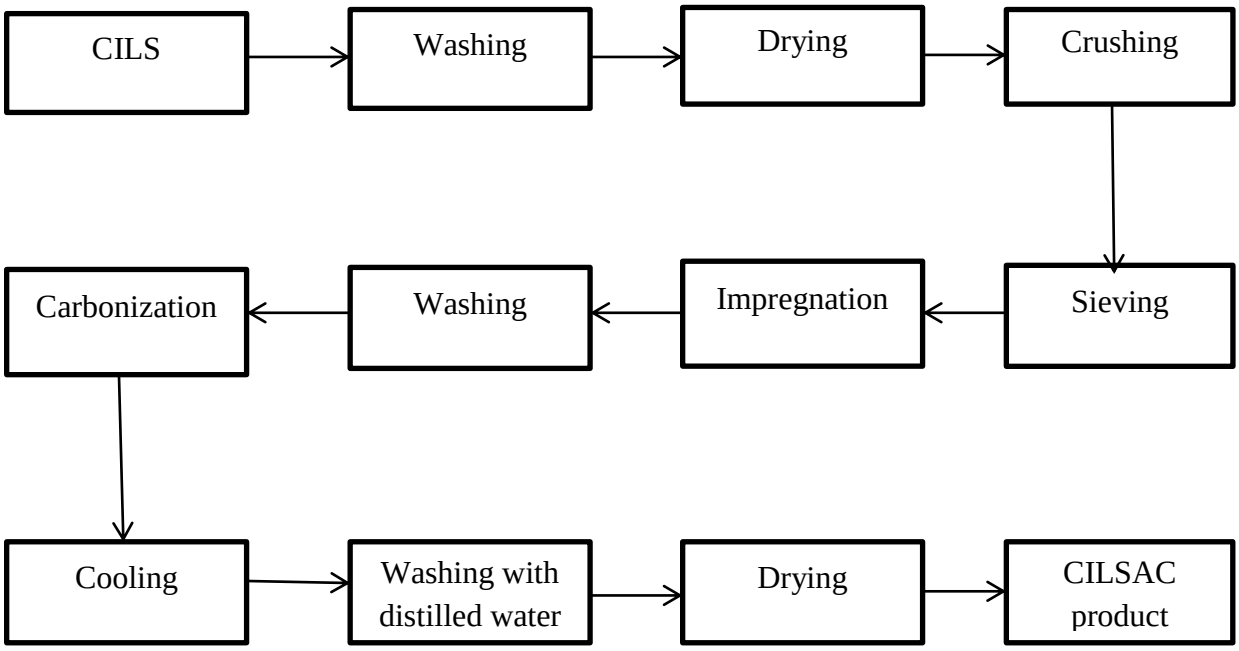

Figure 6: Activated carbon preparation flow diagram

3.4 .Characterization of activated carbon

3.4.1. Proximate analysis of activated carbon

Proximate analysis was performed to determine the amounts of moisture, volatile matter, fixed carbon and ash content in activated carbon.

3.4.1.1. Moisture Content Determination

The moisture content determination was developed by following ASTM (D2867-70) named as Oven-Drying Test Method. A sample of activated carbon (2gm) was placed into a dry, closed capsule and weighed accurately using electronic balance sensitive to 0.0001gm. The capsule opened and placed with the lid in a preheated oven. The sample was dried to constant weight at 105^{o}C for 3hr then removed out from the oven and with the capsule closed, then cooled to ambient temperature. The closed capsule was weighed again accurately.

The moisture content was determined in weight % as follows.

Mc, %= $\frac{w_2-w_3}{w_2-w_1}$ *100……..Eq.3.5

Where, w_1 is weight of capsule with cover (gm), w_2 = weight of capsule with cover plus original sample (gm) and $w_3$is weight of capsule with cover plus dried sample (gm).

3.4.1.2. Ash Content Determination

To determine the total ash content of activated carbon the procedures were followed according to ASTM for activated carbon test method (D 2866-11). First 1g of activated carbon was measured and then placed in the dry and know weight of crucible. Then the crucible was placed in the furnace and it was then ignited at 650^{o}C for 3h. After igniting to the required temperature and time, the crucible was removed out from the furnace and cooled to room temperature and then reweighed. The weight of the ash content was expressed as a percentage of the weight of the activated carbon sample.

Total ash, % = $\frac{D-B}{C-B} * 100$……Eq.3.6

Where, B is weight of crucible (gm), C is weight of crucible plus original activated carbon sample (gm) and D is weight of crucible plus ash sample (gm).

3.4.1.3. Volatile Mater Content Determination

Determination of volatile mater for the activated carbon was conducted according to the procedure specified by ASTM for activated carbon (D 5832-95). The sample was measured carefully and placed in the crucible which was dry, clean and known weight. And then the crucible was closed and placed in the furnace as it was closed to avoid contact between the air and sample. The sample was ignited in the furnace at 950^{o}C for 7min. After seven minute the sample was removed from furnace and cooled to room temperature and then weighted by using electronic balance which was sensitive to 0.0001gm. Then the volatile mater was calculated by using the following equation.

Volatile matter, % = Volatile mater, % = $\frac{\mathrm{D-B}}{\mathrm{C-B}}$ *100……Eq.3.7

Where, D is weight of crucible and ignited sample (gm), C is weight of crucible and original sample (gm) and B is weight of crucible.

3.4.1.4. Fixed Carbon Determination

Fixed carbon was calculated as the resultant summation of percentage of all proximate analysis (moisture content, ash content, and volatile matter content) and subtracted from 100. The fixed carbon was determined by using:

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)...Eq.3.8

3.4.1.5. Carbon Yield

The dried activated carbon was determined before and after carbonization and the carbon yield, Ych, was calculated by using:

$$Y_{ch} = \frac{wf}{wo} * 100 \quad \text{Eq.3.9}$$

Where: w_o, dry weight before carbonization and W_f, dry weight of produced activated carbon

3.4.2. Physico chemical analysis of the activated carbon

3.4.2.1. Bulk Density Determination

Bulk density determination method was conducted according to (Das and Meikap, 2015). Bulk density of the prepared activated carbon was done by water displacement method and was found to be 2.1 gm/10 cm^3. The bulk density was determined by using this equation.

$$Db. = \frac{M}{V} \quad \text{Eq.3.10}$$

Where, m is mass of the sample in gram and V is Volume of the sample measured under test condition in ml

3.4.2.2. Specific Gravity Determination

The specific gravity determination method was implemented (Udeh and Agunwamba, 2017). The relative density pycnometer was cleaned, dried and weighed empty. One third of the activated carbons were put into it and weighed again. The relative density pycnometer was filled with water and reweighed. Finally the pyconometer was emptied, cleaned of the activated carbon particles filled with water alone and weighed.

The specific gravity was determined by using the following formula.

$$Gs = \frac{M2-M1}{(m_2+m_4)-(m_1+m_3)} \quad \text{.....Eq.3.11}$$

Where, M_1 is mass of pycnometer, M_2 is mass of activated carbon inside pycnometer M_3 is mass of dried activated carbon inside the pycnometer fills with water and M_4 is mass of pycnometer filled with water.

The porosity was calculated from equation

$$n = 1-\frac{p}{pwGs(1+w)}$$

Where, n is porosity, P is bulk density, P_w is density of water and w is Moisture content

3.4.2.3. Iodine Number Determination

Iodine number determination was adopted by the following AWWA (B 600-78) powered activated carbon. The sample of activated carbon weighted 1 gram of activated carbon was measured by using electro balance sensitive 0.0001 and transferred in to a dried, glass stopped 250 Erlenmeyer flask then added by pipettes 10 ml of 5% Hcl in to flask and swirl until the activated carbon was wetted then placed the flask on hot- plate brought the contents to the boiled and allowed the boiled exactly for 30 seconds. The allowed the flask and the contents to cooled at room temperature then added by pipette 100 ml of 0.1N Iodine solution. Then stopped the flask immediately and shacked for 30 second then filtered by gravity through a filter paper immediately after 30 second shaking period then discharged the initial 20-30ml of filtrated and collected the remaindered in cleaned beaker then stirred the filtrated in the beaker with glass rod pipette 50ml in to a 250ml Erlenmeyer flask then titrated the 50ml sample with 0.1N sodium thiosulphate solution untilled the yellow color has almost disappeared then added about 1 ml of starch solution and continued titration untilled the blue indicators color just disappeared.

Final recorded the volume of sodium thiosulphate solution used. The Iodine number value was determined as follows.

$$In = \frac{X}{M}A \quad \text{.....Eq.3.12}$$

Where, x is mg of iodine adsorbed by the activated carbon, X is $(12.695N_1) - (279.246N_2V)$, N_1 is normality of iodine solution, N_2 is normality of sodium thiosulphate, V is volume of sodium thiosulphate, M is mass of activated carbon and A is correction

factor depending on the residual normality Nr of filtrate Nr = $\frac{N2V}{50}$, The value of Nr =0.03N, which result is in the range of between 0.008 N and 0.0334 N. Also the correction factor shows in appendix table 3.

3.4.2.4. Point Zero Charge Determination

The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). Determination of point zero charged: the (Farahani *et al*., 2011) test method was adopted. 500ml of 0.1N KNO_3 in the pH range of 2 to 10 was prepared in 9 different flasks. 45ml of KNO_3 solution was taken from the 500ml of KNO_3 solution and initial pH of solution were adjusted by adding drops of 0.5N NaOH and 0.5N HCl solutions and 1gram of activated carbon samples were added to each flask and shacked for 48hours at room temperature. Finally, the pH was measured and recorded. The total charge adsorbed (Δ pH) on activated carbon surface was determined by the difference between pH after 48hr and pH before. The pH values (pH of 2 to 10) are plotted along the x-axis and ΔpH along y-axis, the data obtained from the experiment are plotted and the intersection point is taken as a reference for determining the pH_{PZC} value. The ΔpH value was expressed as follows:

$\Delta pH = pHf - pHi$……Eq.3.13

3.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR study was conducted the activated adsorbent sample to identify the possible surface functional group of the activated carbon before adsorption and then FTIR was also conducted after adsorption consequently the functional group which contribute in the adsorption process was determined by watching the change in frequency as the results of adsorption of Lead on adsorbent using (model IRAffinity-1s) spectrometer in the range wave number between 4000 cm^{-1}– 400cm^{-1} using KBr pellets.

3.6. X-Ray Diffraction (XRD)

X-ray diffraction spectroscopy (XRD) analysis the prepared activated carbon was carried out at Addis Ababa University in departments of chemistry laboratory, using X-ray diffraction instrument (model miniflex 600 PXRD). The X RD pattern of the activated carbon was done to investigate molecular arrangement in the activated carbon. X-ray diffraction technique is power full tool to analyze the crystalline nature of the materials. If the material under investigation is crystalline, well- defined peaks were observed while non- crystalline or amorphous systems show a hollow instead of well- defined peak (Ahmaruzzaman and Bhattacharjee, 2015).

3.7. Batch Adsorption Experiment

3.7.1. Preparation of Stock Solution

Prior to used material was washed with nitric acid and rinsed thoroughly and repeatedly with distill water before use. The required concentrations of working solutions were then prepared from this solution. Lead standard stock solution: dissolve 1.5985 g of lead nitrate ($Pb(No_3)_2$, analytical reagent grade 99.8% $Pb(NO_3)_2$, micro chemical Ltd) dilute to 1 liter in 1 liter volumetric flask. Stopper the flask and mix the solution thoroughly by inverting the flask several times.

This solution contains 1000 ppm Pb (II). Lead standard working solution was prepared by using the following formula.

$C_1v_1 = c_2v_2$.....Eq.3.14

Where c_1 is the initial concentration, c_2 is final concentration, v_1 is initial volume and v_2 is final volume.

All batch experiments were conducted in 250ml Erlenmeyer flask with stopper on a mechanical shaker at 200 rpm, containing 100ml of Pb^{+2} solutions at room temperature (20 ± 1^oC). To evaluated Pb (II) removal efficiency and capacity of the adsorbent (mg/g).To determine the optimum pH of solution to the adsorption, the dose of the adsorbent and the initial concentrations of the metal solutions were investigated based on (Ogunleye *et al*., 2014) by varying any one of the parameters and keeping the other parameter constant.

The sample solution were filtered by using whatman filter paper (0.45 micrometer) at given time. The residual Pb (II) concentrations were determined by Microwave Plasma Atomic Emission Spectrometry (model Agilent mp-aes 4200). All of the experiments were performed in triplicated and the mean values were used. The adsorption at equilibrium, qe (mg/g) was determined by using:

$q_e = (c_o - c_e)\frac{V}{m}$ ……Eq.3.15

Where, c_o and c_e initial and the final (equilibrium) Pb (II) concentration (mg/L), respectively; V is the adsorbate volume (L) and m is the mass of adsorbent used (g)

The percentage of Pb (II) removal was calculated by using:

Removal (%) = $\frac{Co-Ce}{Co} * 100$ …….....Eq.3.16

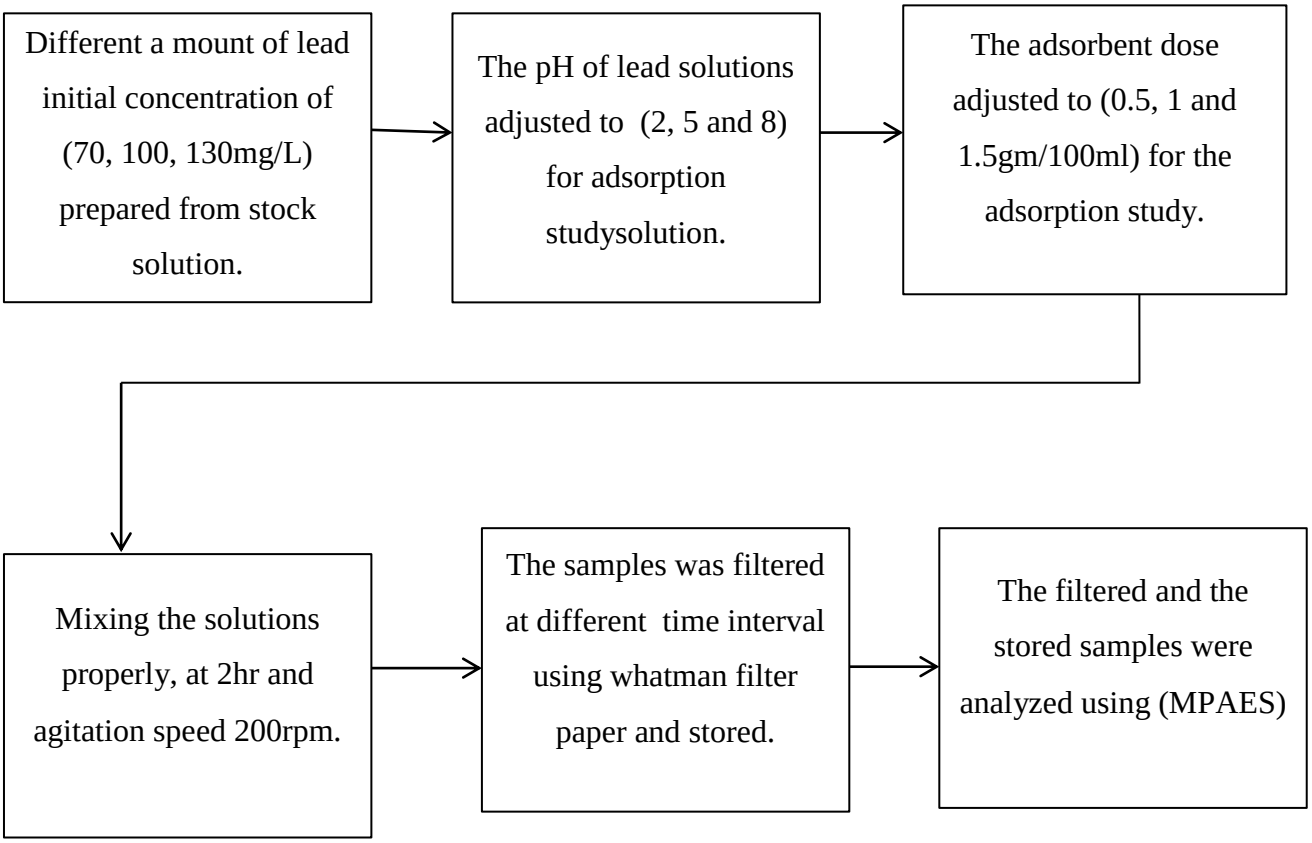

Figure 7: experimental set up of for determination of optimum pH, initial concentration and adsorbent dose.

3.8.4. Factorial Design Methodology

The experimental data were analyzed using a statistical software Design Expert software version 6.0.8. For regression analysis and also for the evaluation of the statistical significance of the equations developed. Design of experiments (DOE) is defined as a statistical technique or approach that is used for the design and the analysis of experiments. The use of DOE is required in designing experiments in order to draw valid and accurate conclusions about any set of experiments. In DOE, a series of tests are made where certain changes are imposed to the input factors, so that the causes of the main changes in the output or response are identified. DOE is a statistical tool used to explore new processes and gain understanding of the existing processes. A full factorial design study is about studying the effect of each of the selected factors on the desired response variable or output. For full factorial designs, three levels of each factor are studied. In this study the set of experimental data were examined using full factorial designs. For the full factorial design three levels considered three factors, pH (A), adsorbent dose (B) and initial concentration (C) are considered to study the main effects and interactions on the removal efficiency and adsorption capacity are response variables.

The factors and the levels of design model are given in table 5. The total numbers of experiments was obtained as 27 run.

Table 5: coded and actual values of the factors on the design experiments**.**

Factors	Name	Unit	Type	Level		
A	pH	-	Numeric	2	5	8
B	Initial. Conc.	mg/L	Numeric	70	100	130
C	Dose	Gm	Numeric	0.5	1	1.5

Sample Digestion

100ml of filtered samples were added in to 250ml conical flask then 10ml of concentrated nitric acid (HN_3) were added to each flask and then boiled on hot plate then the samples were removed from the hot plat and cooled to room temperature after cooling the sample were transferred to 100ml Erlenmeyer flask and filed with distilled water up to the mark to replace water lost due to evaporation.

Microwave Plasma Atomic Emission Spectrometry

To determine the concentration of Pb(II) in sample. Microwave Plasma Atomic Emission spectrometry selected because it was reliable and accurate to measure the concentration of Pb (II). Before measuring the sample. It was required to prepare the sample digestion with concentrated nitric acid because nitric acid is suitable for (MPAES) in addition used to broke down unwanted bond between adsorbent and adsorbant.

Figure 8: Microwave plasma Atomic emission spectrometer

Instrument Calibration

Calibration curve Pb was obtained by using suitable standard solution prepared from stock solution. The quality of result obtained for heavy metal analysis using Microwave plasma Atomic emission spectrometer is seriously affected by the calibration and standard solution preparation procedures. Calibration standards for the element analyzed were prepared in concentration range expected for the analytes in the sample analyzed. In addition, the calibration standards were prepared by taking into consideration the optimum working ranges of the element.

The correlation coefficient (R^2) values that are closer to the absolute value of one indicate that there is a strong relationship between the variables being correlated whereas values closer to zero indicate that there is no linear relationship (Gezahegn, 2013). Can be seen in figure 8 the correlation coefficient of metal was found to be 0.9995 which indicate strong relationship. The correlation coefficient of the element was determined using prepared standards versus their corresponding absorbance. The prepared standard concentration and the corresponding correlation coefficient of the calibration curve for the metal in the wastewater are shown in figure 9. Also the concentration of the working standard solution and the absorbance are presented in table 6

Table 6: Metal Pb Calibration Points Each Component

	Conc. (ppm)	Absorbance
Blank	0	0
Standard 1	5	14543.7483
Standard 2	10	29172.9983
Standard 3	15	44130.2424
Standard 4	20	57204.3578
Standard 5	25	72161.6019
Standard 6	30	85235.71773
Standard 7	35	100192.9614
Standard 8	40	113267.0760

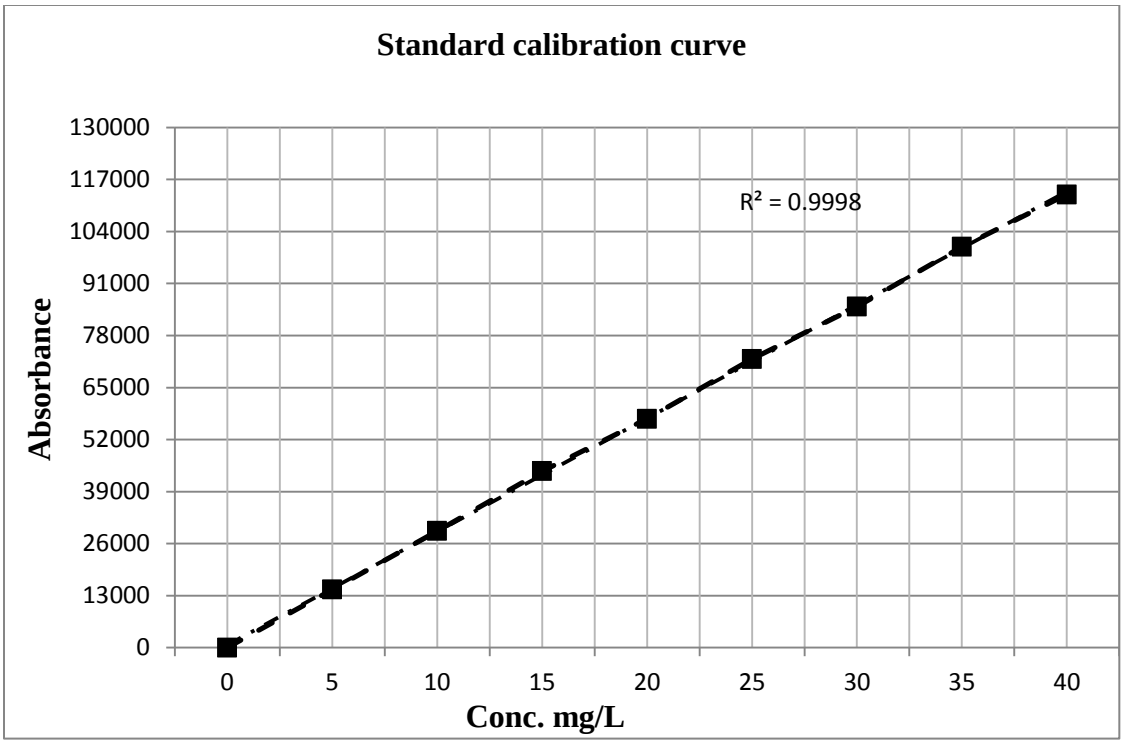

Figure 9: Standard Calibration Curve of Pb (II)

3.9. Determination of Adsorption Isotherm

3.9.1. Langmuir Adsorption Isotherm

The assumption of Langmuir equation includes the following: The molecule are adsorbed on the definities on the surface of the adsorbent, each sites can accommodated only one molecule (monolayer). The area of the site is fixed and its magnitude is determined solely by the geometry of the surface, the adsorption energy is the same at all the site and the adsorption molecules cannot migrated across the surface or interact with the neighboring molecules. The Langmuir isotherm was determined by using.

$$\frac{ce}{qe} = \frac{\text{ce}}{\text{qm}} + \frac{1}{\text{kL qm}} \quad \text{Eq.3.13}$$

Where qm is the maximum amount of metal ion adsorbed capacity (mg/g), qe is the amount of metal ion per unit mass of adsorbent at equilibrium (mg/g), k_L is a constant related to binding energy of adsorption, the constants in the Langmuir isotherm can be estimated by plotting of $\frac{Ce}{qe}$ versu Ce.

The Important Characteristics of Langmuir Isotherm

The characteristics of Langmuir isotherm can be stated in term of dimensionless separation factor and described the type of isotherm. Mathematical it is expressed as follows.

$$R_L = \frac{1}{1+K_L c_o} \quad \text{.....Eq.3.14}$$

Where k_L is the Langmuir constant c_o is metal concentration (mg/L), the value RL indicates the types of isotherm to be either favorable (0<RL<0), unfavorable (RL>0), liner (R_L=1) or irreversible when (R_L=0)

3.9.2. Freundlich Adsorption Isotherm

The Freundlich isotherm equation expressed adsorption on a heterogeneous surface in terms of adsorption, and it can expressed as follows.

$$q_e = k_f ce^{1/n} \quad \text{.....Eq.3.15}$$

Where K_f and n are constants, and n > 1. The Freundlich isotherms are displayed in a logarithmic scale. By taking the logarithmic function of formula above the Freundich isotherm represented as a linear equation:

$$\log qe = logk_f + \frac{1}{n} logc_e \quad \text{.....Eq.3.16}$$

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4. RESULTS AND DISCUSSION

The following section provides the laboratory analysis results of: The activated carbon characterization outcomes, the physico- chemical analysis of Nefas Silk paint factory wastewater parameters, the optimization of parameters such as pH, adsorbent dose and initial concentration for the removal of Pb (II) from aqueous solution and the Canna Indica Linn stem activated carbon for the removal performance of Pb (II), Cu (II), BOD_5, COD, TSS, Turbidity and TDS from paint industry wastewater at the optimum condition and finding another technical data generated from this research.

4.1. Characteristic of Canna Indica Linn Stems Activated Carbon

The result of proximate analysis of adsorbent prepared from canna indica Linn stems are presented in Table 7. The Canna indica Linn activated carbon has the highest fixed carbon content related to the result obtained from cotton stalks (Girgis and Ishak 2010), sugarcane bagasse (Girgis *et al* 2008) and peanut hull (Girgis *et al* 2002). The fixed carbon content value of the canna indica Linn stems activated carbon was 62.90%. This result an indicated in well adsorption of Pb (II). In addition, as observed from Table 8 where the physicochemical property of the adsorbents are presented, canna indica Linn stems activated carbon has the highest iodine number related to the result obtained from banana stalk (Ogunleye *et al.,* 2014) and corn cob (Debela .T, 2016). The iodine value of the canna indica Linn activated carbon was 797.48 (mg/g). The higher value of the iodine number for the canna indica Linn stem activated carbon shows that it has well developed pore structure.

The bulk density contents of the activated carbon obtained was found to be 0.44g/cm^3, an indicate that the bulky material was removed during carbonization. This low bulky density content was desirable more pores were made available for the removal of contaminants from the effluent during the sorption process which involves the diffusion of substance into and on the surface of the cactivated carbon.

Table 7: proximate analysis of the canna indica Linn activated carbon.

Parameter	Moisture	Ashe	Volatile mater	Fixed carbon	Yield of Ac
Value	5.43%	5.00%	26.67%	62.90%	40.00%

Table 8: Physicochemical Properties of the canna indica Linn activated carbon.

Parameter	Specific gravity	Bulky density	Porosity	Iodine number
Value	1.51 (g/cm^3)	0.44 (g/cm^3)	93.00%	797.48 (mg/g)

4.2. Point of Zero Charge Determination

The pH points of zero charge determination of the adsorbent canna indica linn activated carbon was evaluated from the graph of the change in pH versus initial pH for 1gm of the adsorbent. The outcome is presented in figure 10. The graph shows that the value of point of zero charge (pHpzc) was found at 4.25 meaning that has canna indica linn stem activated carbon adsorbent can adsorbed anionic material below the point of zero charge and the adsorbent can adsorbed when the point zero charges above the value of 4.25.

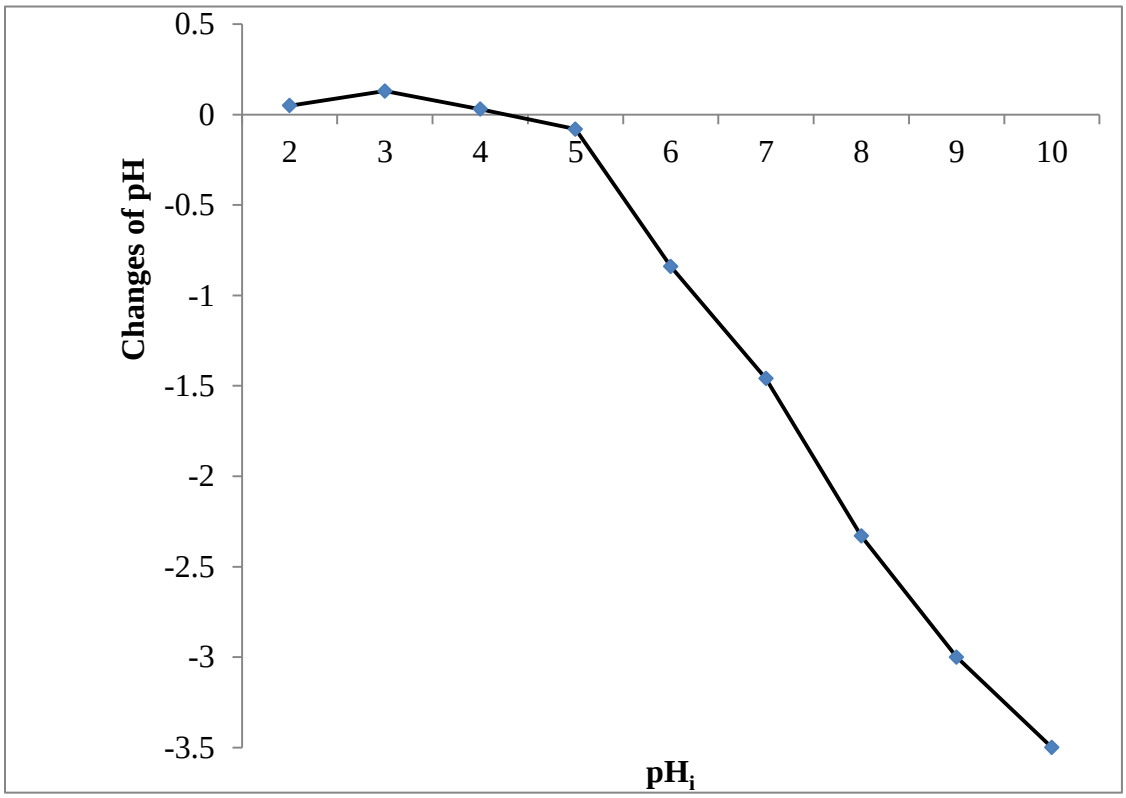
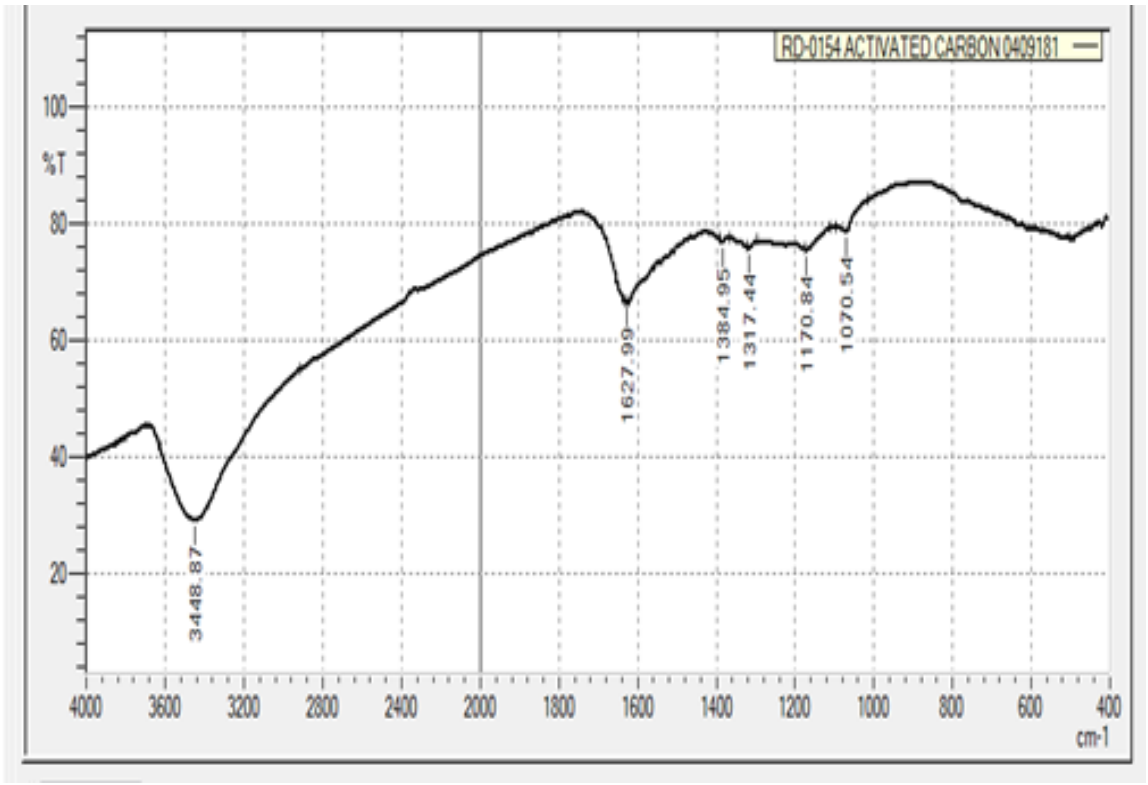


Figure 10: Point of Zero Charge for canna indica linn stem activated carbon (CILSAC)

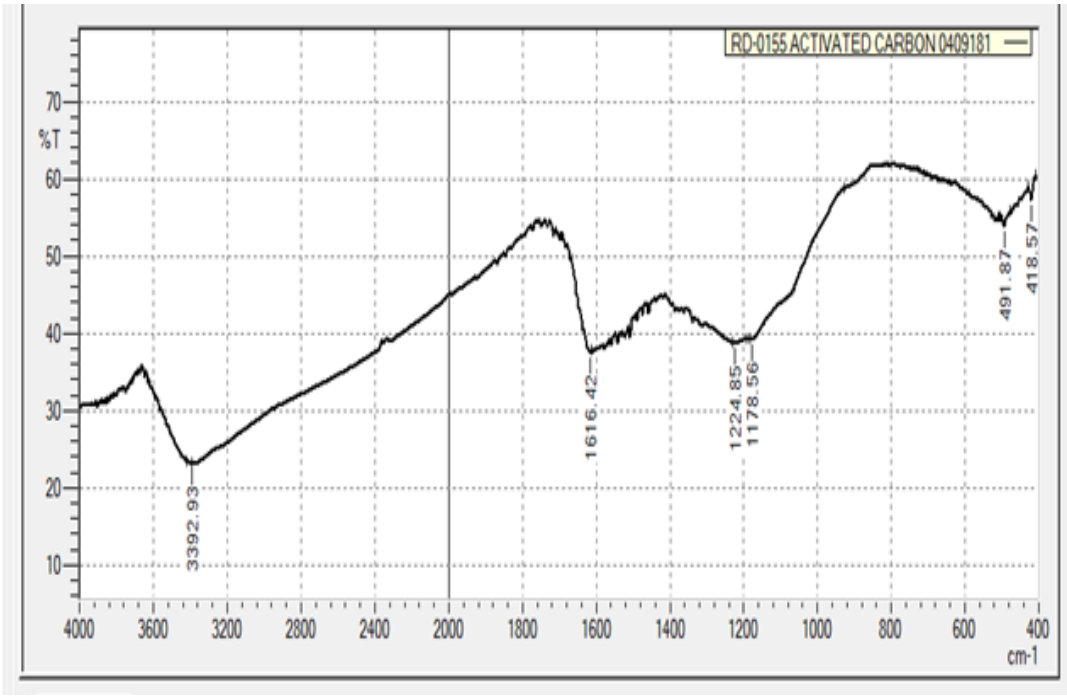
4.3. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR is an important technique to qualitatively determinate the characteristics of the surface functional group, which make the adsorption behavior potential. The FT-IR spectrum of canna indica Linn stem activated carbon was used to investigate the functional groups present on the surface that may be responsible for the removal of heavy metal species. The spectrum of the adsorbent was measured within the range of 4000 - 400cm^{-1} using (model IRAffinity-1S) spectrometer. FTIR spectra before and after the adsorption were compared. Figure (11a) shows that the FTIR spectra of canna indica Linn stem activated carbon (before adsorption) the dominant peaks at 3449cm^{-1}, 1628cm^{-1}, 1385cm^{-1}, 1317cm^{-1}, 1171cm^{-1} and 1071cm^{-1}.

The peaks .region 3449cm^{-1} indicate O-H stretching vibration of alcohol (Agarry *et a*l., 2014), 1628cm-1 indicate C=O stretching (Ogunleye et al., 2014), 1385cm^{-1} indicate C-C stretching vibration in aromatic rings (Somaia *et al*., 2015), 1317cm^{-1} indicate Nitrate (NO_2) symmetric stretching Vibration (Eletta *et al*., 2014) and 1070cm^{-1} indicate CH bending vibration of C-H_2 and C-H_3. After adsorption of Pb(II) the dominant peaks shit in to 3449cm^{-1} to 3393cm^{-1}, 1627cm^{-1} to 1616cm^{-1}, 1385cm^{-1} to 1225cm^{-1}, 1317cm^{-1} to 1179cm^{-1}, 1170cm^{-1} to 492cm^{-1} and 1071cm^{-1} to 419cm^{-1}. Shifting was observed on C-C stretching and C-N stretching. After Pb (II) binding, a change of peak position occurs indicating the change in the environment of these groups. The shift in the wavelength corresponds to the change in the energy of functional groups that indicates the existence of a Pb binding process done on the surface.



(a)



(b)

Figure 11 : FTIR (a) Before And (b) After Adsorption

4.4. X-Ray Diffraction (XRD)

The x-ray diffraction pattern of the canna indica Linn activated carbon as shown in figure 12. The x-ray diffraction pattern analysis on the activated carbon can be observed two peaks at angle 35.5^0 and 40^o respectively shows that the crystalline carbonaceous structure. The peak is produced due to better layer alignment which is the characteristic of a crystalline. The absence of sharp peak shows that the major parts of the activated carbon is amorphous, which is an advantage property for a good adsorbent (Kennedy *et al*., 2009).

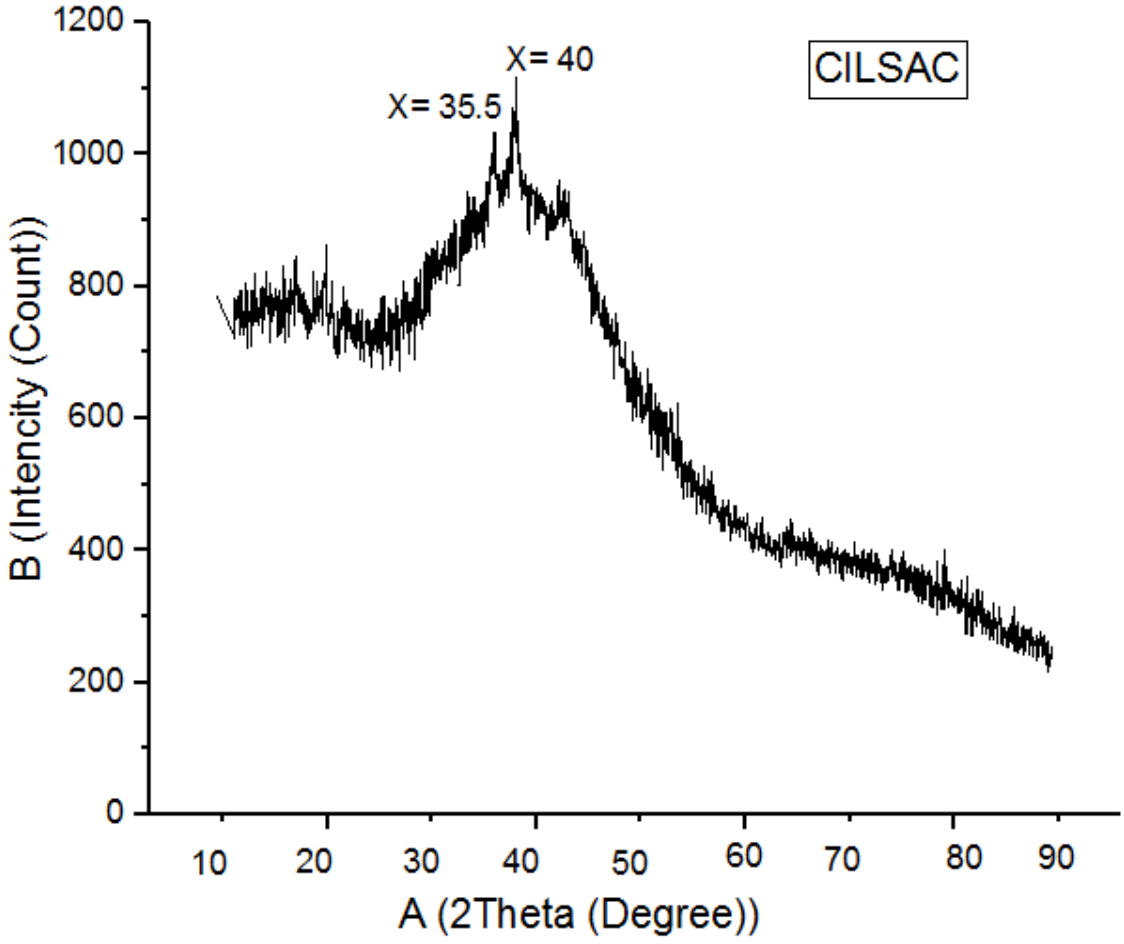


Figure 12: X-RD Of The Canna Indica Linn Stem Activated Carbon

4.5. Characteristic of Nefas Silk Paint Factory Wastewater

The Paint wastewater samples were taken from Nefas silk paint factory from the equalization tank for three times in five day interval. The next table shows some of the selected physico-chemical parameters of paint wastewater quality before application of adsorption.

Table 9: Physicochemical Characterization of the Untreated Paint Effluent**.**

parameters	Mean ± SD mg/L	Max value (mg/L)	Min value(mg/L)	Max permissible limit (mg/L)
pH	5.38 ± 1.24	6.40	4.00	6 -9
Temperature (^{o}c)	20.6o ± 1.42	22.20	19.50	40
Turbidity (NUT)	2791.33±18	2900.00	2588.00	25
BOD_5 (mg/L)	171 ± 16.80	190.00	159.00	50
COD (m/L)	2401.70 ±7.64	2410.00	2395.00	150
DO (mg/L)	0.18 ±0.08	0.25	0.09	5-20
TSS (mg/L)	619 ±56.31	696.00	558.00	50
TDS (mg/L)	577.33 ±59.50	620.00	520.00	*
Pb(II)	2.95 ±0.17	3.02	2.75	0.5
Cu(II)	1.95 ±0.17	2.15	1.95	1

The untreated wastewater as shown in table 9 above, the results indicate that highly polluted effluent, for example the Pb (II) value was 2.95 mg/L as against the maximum limited Pb (II) which is 0.50 mg/L as stated by EEPA (2003). It may cause effects on environment, human and animal life through ecological food chain. It has carcinogenic and mutagenic property which may cause to cancer, reduced mental and central nervous function. Lead is a toxic metal that causes adverse effects on both human health and the environment. While lead exposure is also harmful to adults, lead exposure harms children at much lower levels, and the health effects are generally irreversible and can have a lifelong impact ((WHO. 2015) The younger the child, the more harmful lead can be, and children with nutritional deficiencies absorb ingested lead at an increased rate. The human fetus is the most vulnerable, and a pregnant woman can transfer lead that has accumulated in her body to her developing child. Lead is also transferred through breast milk when lead is present in a nursing mother (WHO, 2010). The other parameters such as pH, DO, BOD_5, COD, TSS, TDS and turbidity were above the limit for effluent discharge, and these may cause effects on aquatic life due to limits light penetration, Covers aquatic animals and plant and brings insoluble toxins into water bodies (Al-Rekabi et al 2007).

4.6. Batch Adsorption Studies

The equilibrium adsorption capacity and removal efficiency were determined by using equation (3.15) and equation (3.16) stated in methodology section

$$q_e = \frac{c_o - c_e}{M_{ac}} * \mathrm{V}$$

$$\mathrm{E}\ (\%) = \frac{C_O - C_e}{c_o} * 100$$

Where, qe (mg/g) is equilibrium adsorption capacity, c_o(mg/L) is the initial concentration of Pb (II) in the solution, c_e (mg/L) is the equilibrium concentration of Pb (II) in the solution, V (L) is the volume of the Pb (II) solution and E (%) is the removal efficiency.

The average of three replication batch tests obtained results is presented in Table 10 and the discussion of the result obtained from batch study is described below the table in detail.

Table 10: Experimental design and results according to the 3^3 full factorial design.

	Factors				Response	
Run	pH	Initial Conc. (mg/L)	Adsorbent Dose (gm)	C_e(mg/L)	Average removal (%)	Average q_e (mg/g)
1	2	70	0.5	13.517	80.6900	11.2966
2	2	100	0.5	23.9315	76.0000	15.2137
3	2	130	0.5	39.1036	69.9200	18.17923
4	2	70	1	11.1957	84.0000	5.8804
5	2	100	1	15.3798	84.6200	8.462
6	2	130	1	26.7909	79.3900	10.3209
7	2	70	1.5	7.8789	88.7400	4.1414
8	2	100	1.5	13.8123	86.200	5.7458
9	2	130	1.5	18.2815	85.9300	7.4479
10	5	70	0.5	3.667	94.7600	13.2666
11	5	100	0.5	6.2218	93.7700	18.7556
12	5	130	0.5	10.3241	92.0000	23.9351
13	5	70	1	3.1708	95.4700	6.6829
14	5	100	1	6.0847	93.9000	9.3915
15	5	130	1	7.6887	94.0000	12.2311
16	5	70	1.5	2.0152	97.1200	4.5323
17	5	100	1.5	4.7977	95.2000	6.3468
18	5	130	1.5	6.8001	94.7700	8.2133

19	8	70	0.5	5.9546	91.5000	12.8091
20	8	100	0.5	11.7025	88.2900	17.6595
21	8	130	0.5	30.0732	76.8600	19.9854
22	8	70	1	4.3759	93.7400	6.5624
23	8	100	1	10.8597	89.1400	8.914
24	8	130	1	15.2375	88.2800	11.4763
25	8	70	1.5	3.0009	95.7000	4.4661
26	8	100	1.5	5.4494	94.5500	6.3033
27	8	130	1.5	7.8348	93.9700	8.1443

4.6.1. Effects of pH on the Removal of Pb (II)

Effects of pH on a solution are major factor used to determine the adsorption property of an adsorbent from wastewater. The possible reasons are its effects on the chemistry of the ions and the activity of functional groups (carboxylate, phosphate and amino groups) on the surface of the adsorbent (Reddad *et al*,. 2002). In this study the effects of pH were tested by changing pH of solution in the range of 2, 5 and 8 at constant intial concentration of 70mg/L and constant adsorbent dose of 1.5gm.

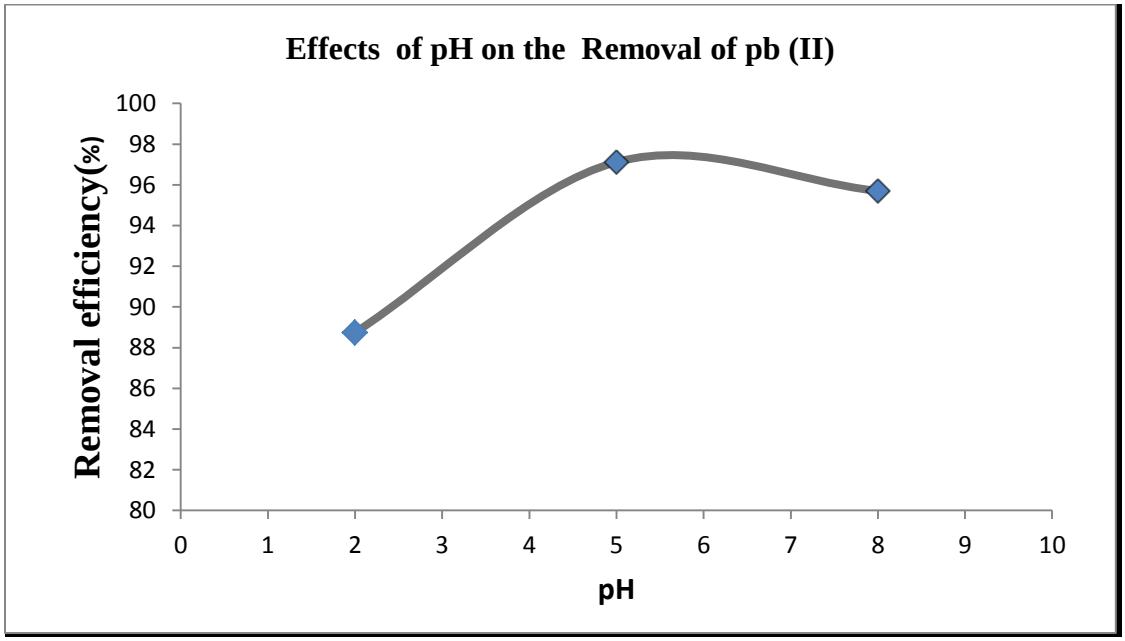


Figure 13: Effects of pH on the removal efficiency: contact time =2hrs, rpm = 200, Conc. = 70 mg/L, Dose = 1.5 g and T = 25^{o}C

From figure 13, the percentage removal of Pb (II) ions increased from 88.74% to 97.12%, when the pH of the solution was correspondingly increased from 2 to 5. Because at low pH values, the adsorbent is positively charged since the pH is lower than the point of zero charge (PZC) (Mwangi and Ngila, 2012). Hence the removal efficiency of Pb (II) ions is very low due to the electrostatic repulsion forces between positive charged H_3O^+ and the Pb (II) ions (Gundogdu *et al*., 2009). Therefore when the value of pH increased from 2 to5 the concentration of hydronium ion was decreased which favorable Pb (II) approaching to the active site of the adsorbent. In this reason the removal efficiency increased.

On the other hand the percentage removal efficiency was decreased from 97.12% to 95.70% when the values of pH increased from 5 to 8. Because the formation of (Pb $(OH)_2$) and soluble hydroxyl complexes such as $PbOH^+$, aqueous $Pb(OH)_2$, and $Pb(OH)^{3-}$ and the activated carbon was deteriorated with the accumulation of Pb (II) ions making true adsorption studies impossible (Zayat and Smith, 2006). Related trends were reported for adsorption of Pb (II) ions on the activated carbon prepared from coconut shell (Sekar. M, 2004). Sawdust (Ayyappan et al,. 2005), coffee husk (Nadeem et al,. 2006). Therefore pH 5 was selected as optimum for further studied.

4.6.2. Effects of Adsorbent on the Removal of Pb (II)

The adsorbent dosage is an important parameter in the adsorption studies because it determines the capacity of the adsorbent for a given initial concentration of Pb (II) solution (Auta and Hameed, 2012). For this study the effect of dosage were investigated by changing the adsorbent in range 0.5, 1 and 1.5gm and at constant initial concentration of 70mg/L and constant pH of 5. The result from figure 14a. Shows that the removal of Pb (II) increased from 94.74 % to 97.12 % with increasing adsorbent dose from 0.5 to 1.5gm respectively. This is because for a fixed initial metal concentration, while increasing the adsorbent dose provides a greater adsorption sites.

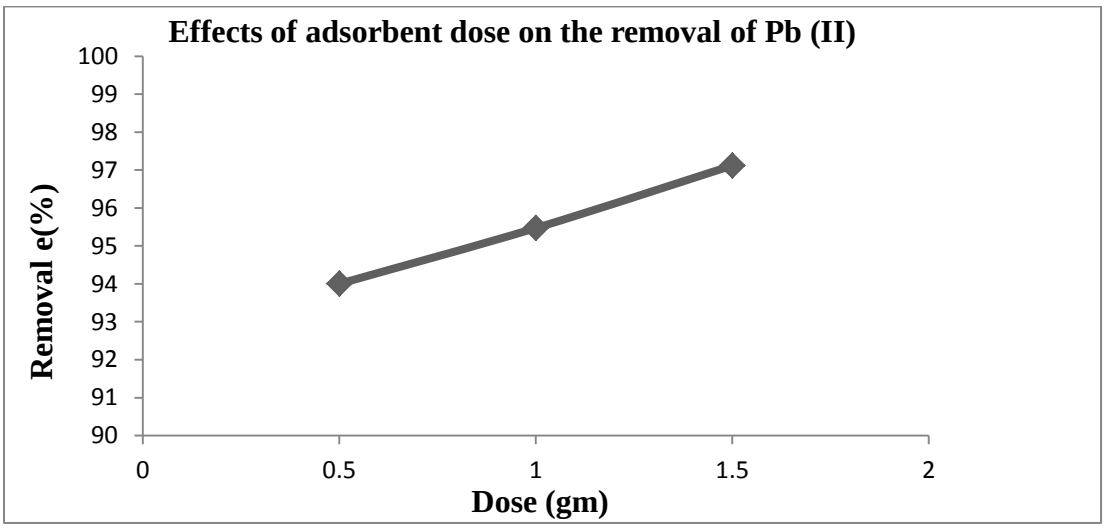


Figure 14a: Effect of Adsorbent Dose on Removal Efficiency: pH = 5, Contact Time = 2hrs, C= 70 mg/L, T 25^{o}C, rpm = 200.

A reverse trend was observed with adsorptive capacity which decreased as the adsorbent dosage was increased (figure15b). Similar results were reported (Udeh and Agunwamba, 2017) in removal of Pb (II) from aqueous solution using bamboo based activated carbon as adsorbent. This result can be described to the fact that some of the adsorption sites remain unsaturated after the adsorption process. Even if the up-take of the metal increased by increasing the adsorbent dose, beyond a dose of 1.5 gm and the rise of the adsorption efficiency is insignificant and the capacity of adsorbent is very low. The removal of lead (II) increased with an increase in the adsorbent dosage up to a certain level and then it remains almost constant. This is expected because of the increase in the adsorbent surface. Therefore 1.5 gm of adsorbent was taken as an optimum dose for further experiment.

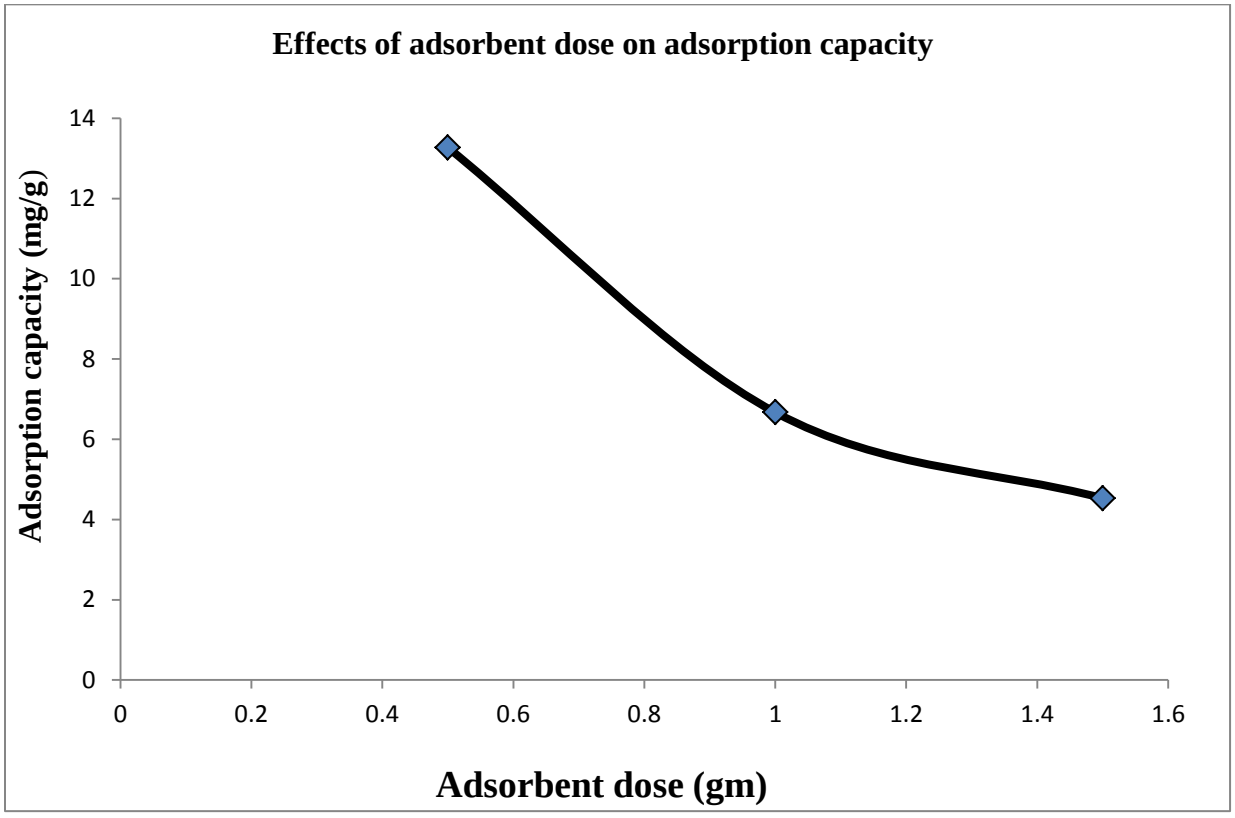


Figure 15b: Effect of Adsorbent Dose on Adsorption Capacity: pH =5, Contact Time = 2hrs, C=70mg/L, rpm= 200, T = 25^{O}C.

4.6.3. Effects of Initial Concentration on the Removal of Pb (II)

The initial Pb (II) concentration played important role on the adsorption capacity of Pb (II) on the adsorbent. The effects of the initial Pb (II) concentration on the adsorption removal were studied by changing the value of initial concentration Pb (II) in range of 70, 100 and 130 mg/L and at constant adsorbent dose of 1.5gm and at constant pH of 5.

The result in figure.16a, the percentage of removal decrease from 97.12% to 94.77 % as the initial concentration is increase from 70 to 130 mg/L. Because low concentration there is low number of lead ion to the ration of surface active site that found in the adsorbent surface. Therefore, all of lead ion may interact with the active site. In contrast when higher initial concentration proved more lead ion for attached on adsorbent surface. As results the active site is not sufficient and saturation in the adsorbent was happened. Therefore this is resulting for the reduction of in percentage removal.

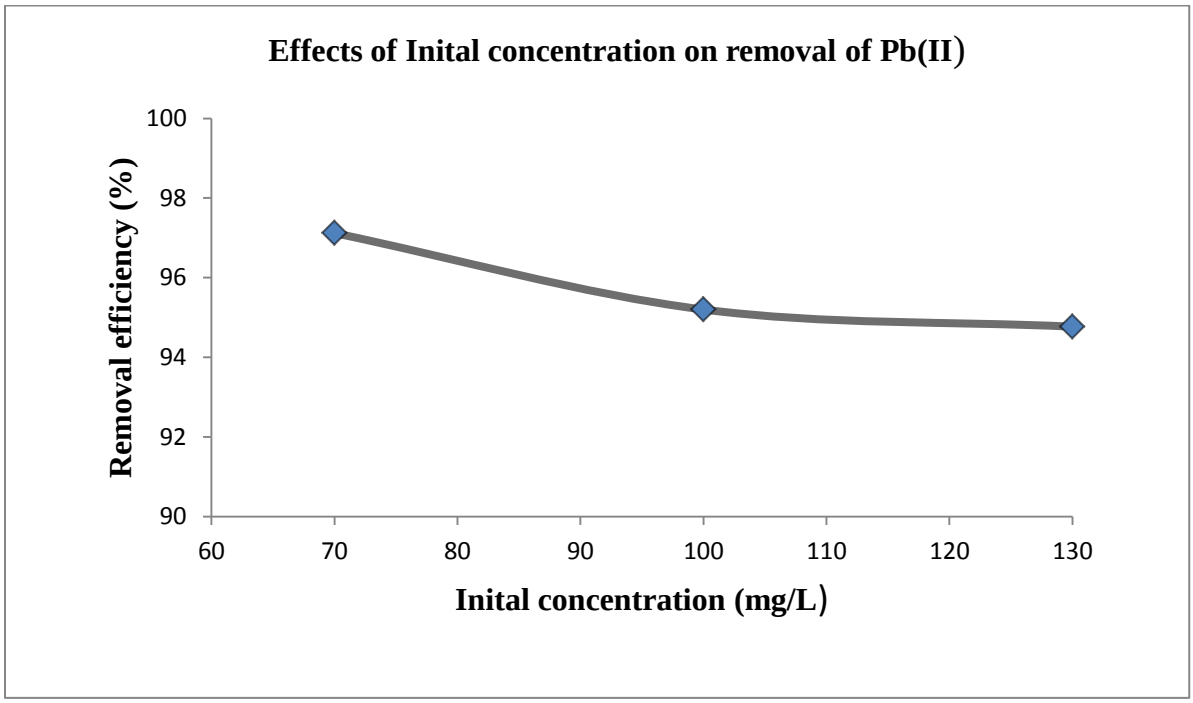


Figure 16a: Effects of Initial Concentration on Removal Efficiency: pH = 5, Dose 1.5g, T= 25^{o}C rpm = 200 and Contact Time =2hrs.

On the other hand by increasing the initial Pb (II) concentration, the adsorption capacity was increased from 2.0152 mg/g to 6.8001 mg/g with increasing initial concentration from 70 to 130 mg/L (figure.17b). Because the higher initial concentration of provided the higher initial concentration of Pb (II) provided an additional driving force to overcome the mass transfer resistance for Pb (II) transfer between the solution and the surface of the adsorbent (Yao *et al*., 2011).

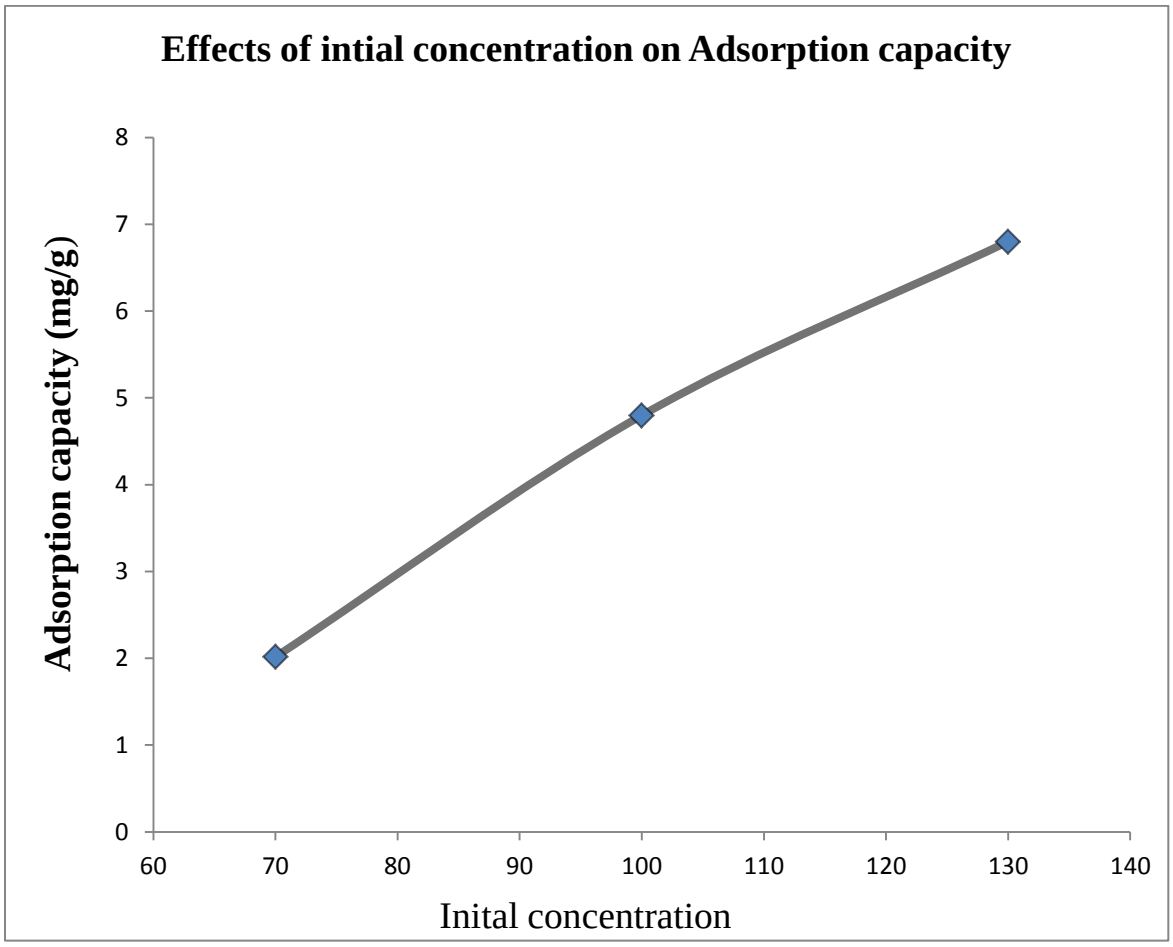


Figure 17b: Effects of Initial Concentration on Adsorption Capacity Contact Time = 2hrs, pH = 5, Dose 1.5 g, Conc. = 70mg/L, rpm = 200 and T =25^{o}C

4.7. Statistical Analysis of experimental results

4.7.1. Effects of individual factors and their interactions

Analysis of variance of the quadratic regression model was a significant model, from evident of fisher's F test with a very low probability value [(p-model>F) = 0.0001]. Appendix table 5.1 shows that the individual effects of factors on the removal efficiency of Pb (II) by pH and adsorbent dose more than the initial concentration based on the F-values of 41.95 pH, 38.06 adsorbent dose and 21.45 initial concentration.

The quadratic effects of F-value of pH (66.92) and the adsorbent dose (0.52) more than the initial concentration (0.055). The interaction effect of the pH - adsorbent dose was meaning full having F-value of 5.53. The interaction effect of pH-initial concentration and adsorbent dose- initial concentration shows very low F-value of 0.015 and 0.55 respectively. The next Figure 18 shows the 3D and contour plots, the combined effect of pH and adsorbent dose for the removal efficiency of Pb (II) at a constant initial concentration of 70mg/L, contact time of 2hr, temperature of 25^{o}C and rpm of 200. The result from figure 18 shows that the removal efficiency of Pb (II) increased with increasing pH from 2 to 5 with increasing the adsorbent dose from 0.5 to 1.5gm and then decreased, when further increasing pH from 5 to 8.

Appendix table 5.2 shows that the three factors of pH, initial concentration and adsorbent dose on the adsorption capacity. The pH has the least effect base on its F-value which has smaller (8.11) and also it's the variation did not have a significant effect on the process. The individual factors of adsorbent dose and initial concentration as well as their interaction had the most significant effects on the adsorption capacity can be seen by the F-values of 169.91, 575.43 and 18.61 respectively. The 3D and the contour plots which were constructed to show the most significant two factors of adsorbent dose and initial concentration on the adsorption capacity at a constant pH of 5, contact time of 2hr, temperature of 25^{o}C and rpm of 200 shown in figure 19. From these figure can be observed, the adsorption capacity decrease with increasing in the adsorbent dose from 0.5 to 1.5gm as well as increasing in initial concentration from 70 to 130mg/L. Increasing the adsorbent dose provides a greater surface area or available adsorptions sites increases and therefore result in the increase of the amount of Pb (II) adsorbed.

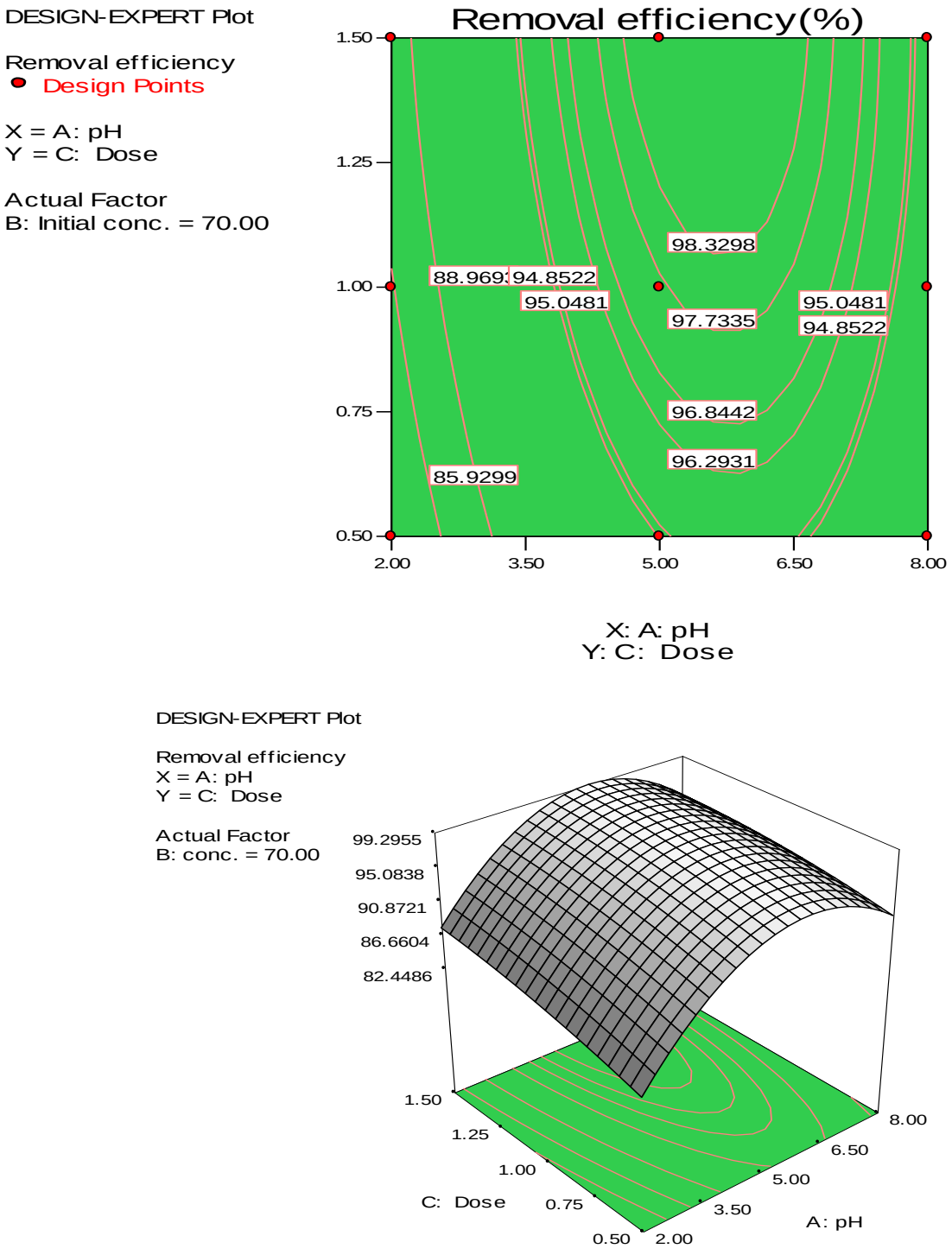
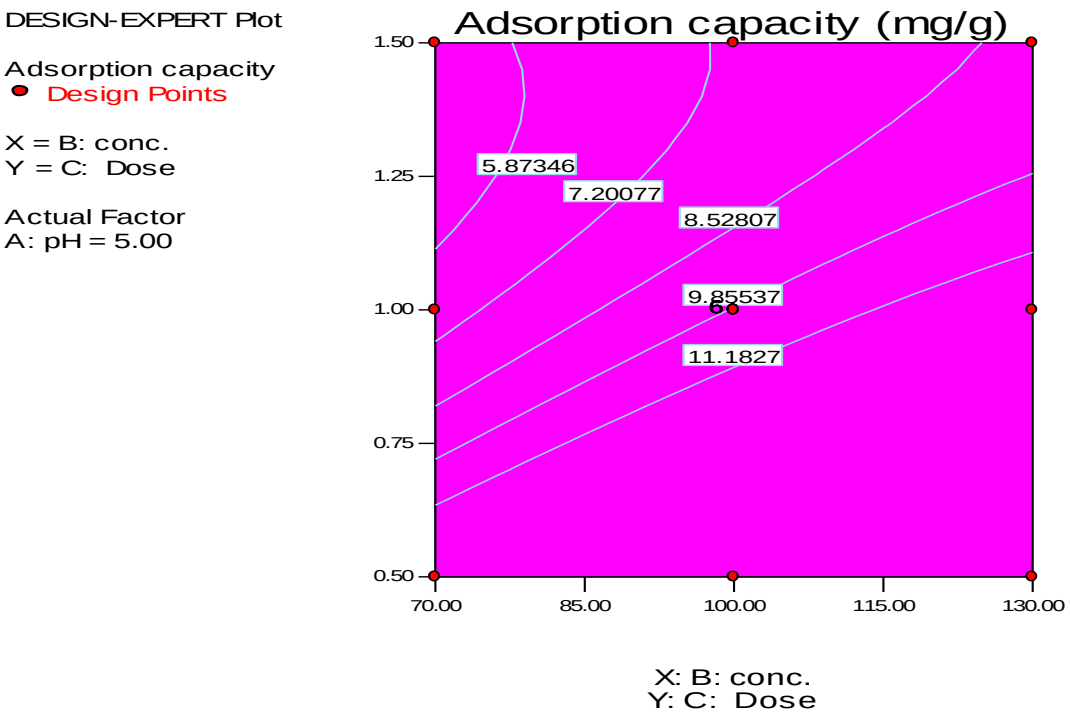


Figure 18: The combined effects of pH and adsorbent dose on the removal efficiency of Pb (II) with initial concentration fixed at zero level (c_o =70).



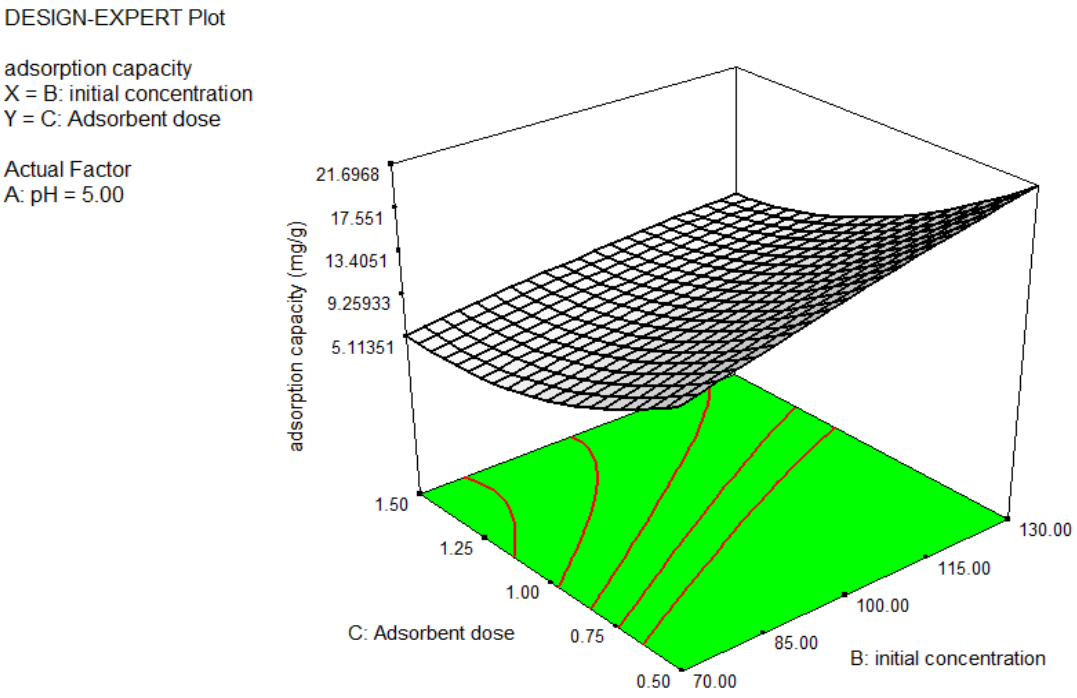


Figure 19: The combined effects of Initial Concentration and Adsorbent Dose on the Adsorption Capacity with pH fixed at zero level (pH = 5).

4.8. Adsorption Isotherm

The results obtained on the adsorption of Pb (II) ions with different initial concentration (70, 100 and 130mg/L) and fixed adsorbent dose (1.5gm) and pH (5) were studied by using the models of Langmuir and freundlich which correspond to homogenous and heterogeneous adsorbent surfaces respectively.

4.8.1 The Langmuir's Isotherm

The Langmuir's isotherm calculated using equation 3.13 stated in methodology section and the results are shown below in the table 10.

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{klqm}$$

Table 11: Langmuir Isotherm for Adsorption Pb (II) Using CILSAC

c_e	q_e	c_e/q_e
2.0152	4.533232	0.444628
4.977	6.33486	0.785652
6.8001	8.2133	0.827934

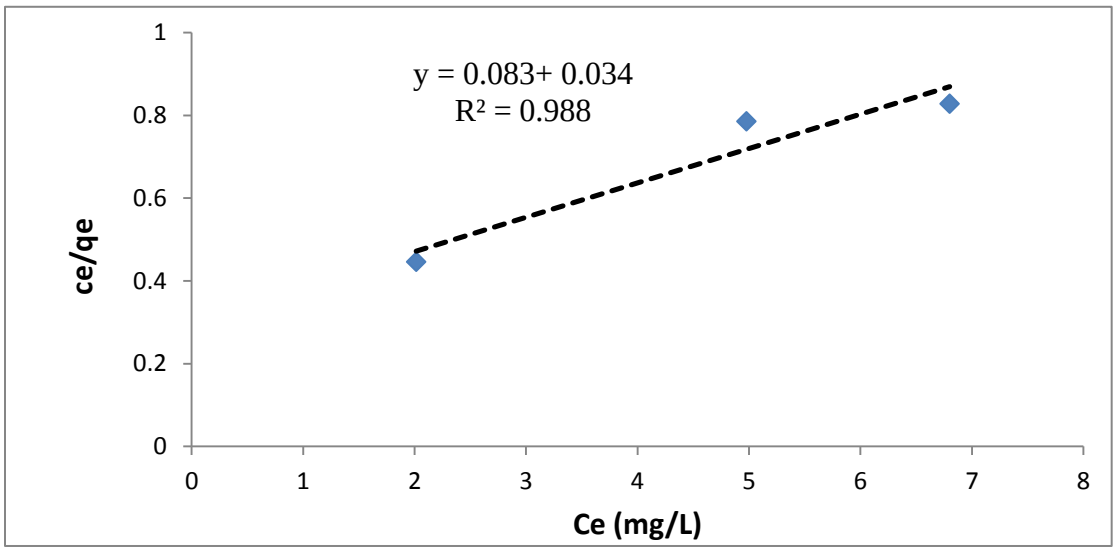


Figure 20: Langmuir Adsorption Isotherm for Adsorption of Pb (II) on the CILSAC: pH =5, T = 25^{o}c, Dose = 1.5, contact time 2hrs and rpm =200.

Figure 20 gives the linear plot of ration of equilibrium concentration to mass of adsorbent versus equilibrium concentration. The plot has R^2 value of 0.988 with a slope and intercept values of 0.083 and 0.305 respectively. The values of the Langmuir constants ($k_L$and q_{max}) for adsorption of Pb (II) ion using canna indica Linn activated carbon were determined from the slope ($1/q_m$) and intercept ($1/q_m\ k_L$). The values of q_{max} and k_L were 12.000 (mg/g) and 0.240 (L/mg) respectively.

The favorability and feasibility of adsorption process can be determined by the separation RL in the analysis data by Langmuir isotherm it is given by equation (3.12)

$$R_L = \frac{1}{1+K_L c_o}$$

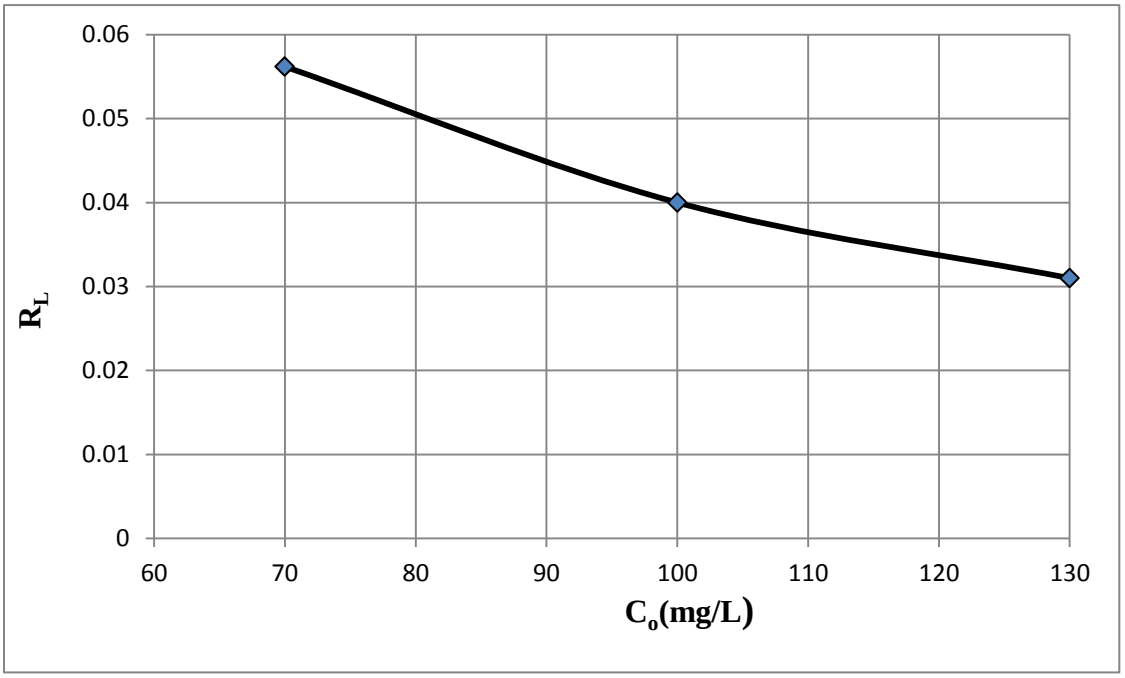


Figure 21: Plot of Separation Factor Versus Initial Pb (II) Concentration

Figure 21 showed that the shape of the isotherm depends on the value of RL. The isotherm is unfavorable (R_L>1), linear (R_L=1), favorable (0< R_L<1) or reversible (R_L= 0). The initial concentration increase, R_L value is closer to zero which is due to effective of pore diffusion adsorption process. Therefore, the type of adsorption process of Pb (II) on to the canna indica Linn stem activated carbon was favorable.

4.8.2. The Freundlch Isotherm

The freundlich adsorption isotherm were displayed in a logarithmic scale by taking the logarithm equation (3.16) and the result are shown below in table 11

$$\text{Log}q_e = \text{Log}k_f + \frac{1}{n}\text{Log}c_e$$

Table 12: Freundlich Isotherm For Adsorption Of Pb (II) Using CILSAC.

Ce	qe	Ce/qe	logqe	Logce
2.0152	4.5332	0.44463	0.65640	0.30432
4.7977	6.33486	0.75735	0.80174	0.69697
6.8001	8.2133	0.827934	0.91518	0.832552

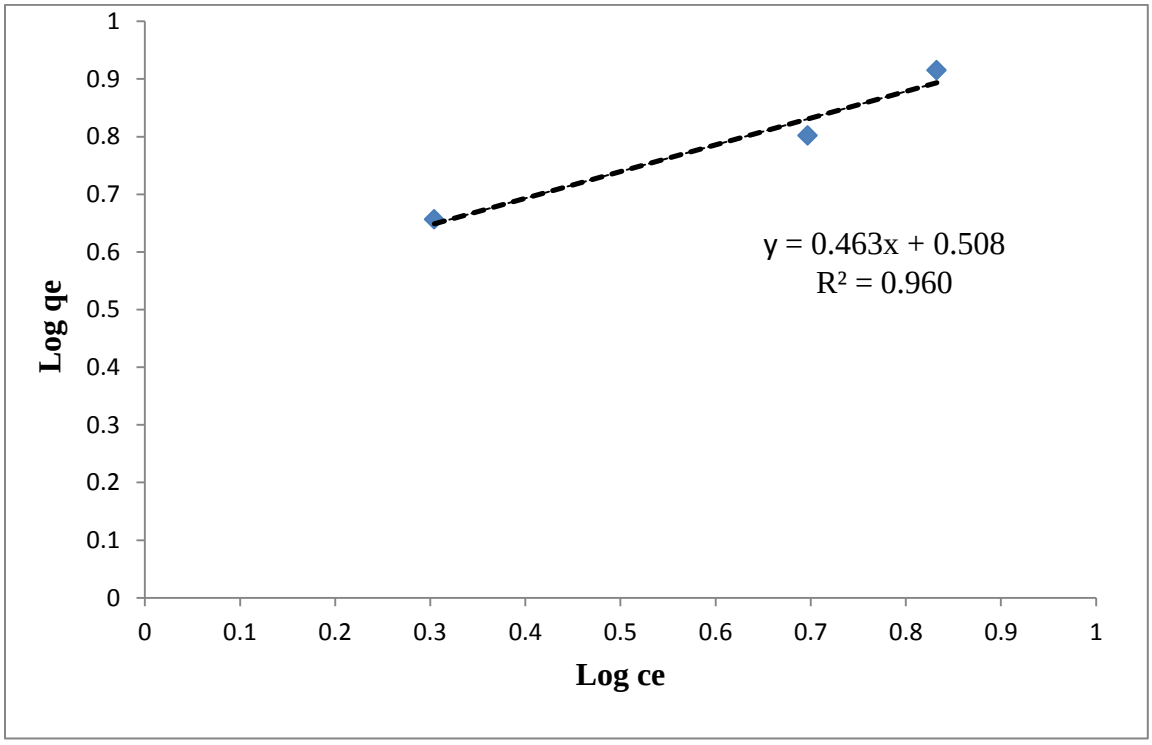


Figure 22: Freudlich Adsorption Isotherm Adsorption of Pb (II) on CILSAC: at pH = 5, contact time 2hrs, Dose = 1.5g, T =25^{o}c and rpm 200.

The next table 13 presents the values of equilibrium concentration, c_e the amount adsorbed $q_e$and the logarithm c_e and q_e at various initial concentrations of Pb (II) and the other variable kept constants. From figure 21 showed that the liner plots of logq_e versus log $c_e$with R^2 Value of 0.960, with the value of slope and intercept of 0.463 and 0.508 respectively. The value of the freundlich constants (k_f and n_f) for the adsorption of Pb (II) onto the canna indica Linn stem activated carbon obtained from the plot were 3.200 and 2.200 respectively.

Table 13: Langmuir and Freundlich Isotherm constants and coefficient regression, R^2 for Pb (II) Adsorption using CILSAC.

Langmuir isotherm constants			Freudlich isotherm constants		
q_{max}(mg/g)	k_L(L/mol)	R^2	k_f(mg/g)	n	R^2
12.000	0.240	0.988	3.220	2.200	0.960

Table 13 displayed that the adsorption constants of Langmuir and Freudlich for Pb (II) ions adsorption onto canna indica Linn activated carbon resulting from the two linear isotherms. The values of q_{max} (mg/g) and K_L (L/mol) were obtained from Langmuir isotherm plot, with the high value coefficients of regression R^2 = 0.98705 and the value of k_f (mg/g) and n were obtained from Freudlich isotherm plot, with the high value coefficients regression R^2 = 0.0.960. The correlation coefficient (R^2) Langmuir equation gives a better fit to the adsorption isotherm than the Freundlich. The Freundlich constants n gives an indication of the favourability of sorption. In Table 11 the values of n for Pb (II) adsorption were 2.2 for canna indica Linn stem activated carbon. According to (Chen et al., 2010) values of n, (which reflects the intensity of adsorption) ranging between 2 and 10 represents favourable adsorption. So, the results obtained are consistent with the requirement for favouarable adsorption since they were within the range of 2 to 10.

The Removal Performance of Canna Indica Linn Stem Activated Carbon.

After optimization analyses were conducted for the synthetic wastewater by Pb (II) removal efficiency, the analysis were conducted from Nefas silk paint industry waste water by the removal of Pb (II), Cu (II), BOD5 , COD, TSS, TDS and turbidity at the optimum condition of Pb (II) removal from synthetic wastewater.

Table 14: Optimum conditions of Pb (II) Removal from Synthetic wastewater : at constant, T =25^{o}C, rpm = 200, Contact Time =2hr

pH	Adsorbent dose (gm)	Removal efficiency (%)
5	1.5	97.12

Using optimum condition for the removal of Pb (II) from synthetic wastewater in Table 14 above, the removal of Pb (II) and other competitive pollutants were evaluated from Nefas silk paint industry wastewater by using 1.5gm of activated carbon per 100 ml of wastewater. Table 14 presents some of the selected physico- chemical analyses of wastewater were carried out after application adsorption.

Table 15**:** Physiochemical analysis of the treated paint effluent

Parameter	Treated wastewater
pH	6.9
Temperature (^{o}C)	20
Turbidity (NUT)	10.966
BOD_5(mg/L)	25
COD (mg/L)	150
DO (mg/L)	9.2
TSS (mg/L)	138
TDS (mg/L)	176
Pb (mg/L)	0.428
Cu (mg/L)	0.168

The treated wastewater as shown in table 15 above, the results indicate an appreciable improvement on the quality of the water. The pH value changed from 5.38 to 6.9, dissolved oxygen increased from 0.18 mg/L to 9.20 mg/L while the biological oxygen demand, chemical oxygen demand, total suspended solid, total dissolved solid, lead, copper and turbidity were reduced from 171 mg/L to 25 mg/L, 2401.70 mg/L to 150.00 mg/L, 619.00 mg/L to 138.00 mg/L, 577.33 mg/L to 176.00 mg/L, 2.95 mg/L to 0.428 mg/L, 1.95 to 0.168 mg/L and 2791.33 NUT to 10.966 NUT respectively.

Figure 23 shows that the canna Linn stems activated carbon the removal efficiency of Pb (II) from real wastewater and synthetic wastewater at the optimum condition. The initial measured concentration of Pb (II) from real wastewater was taken 2.95 mg/L. After application of adsorption was found to be 85.30 % of Pb (II) removal efficiency. This result lower than the removal efficiency of synthetic wastewater because of the presence of other competitive pollutants in the real wastewater that affect the removal efficiency the activated carbon.

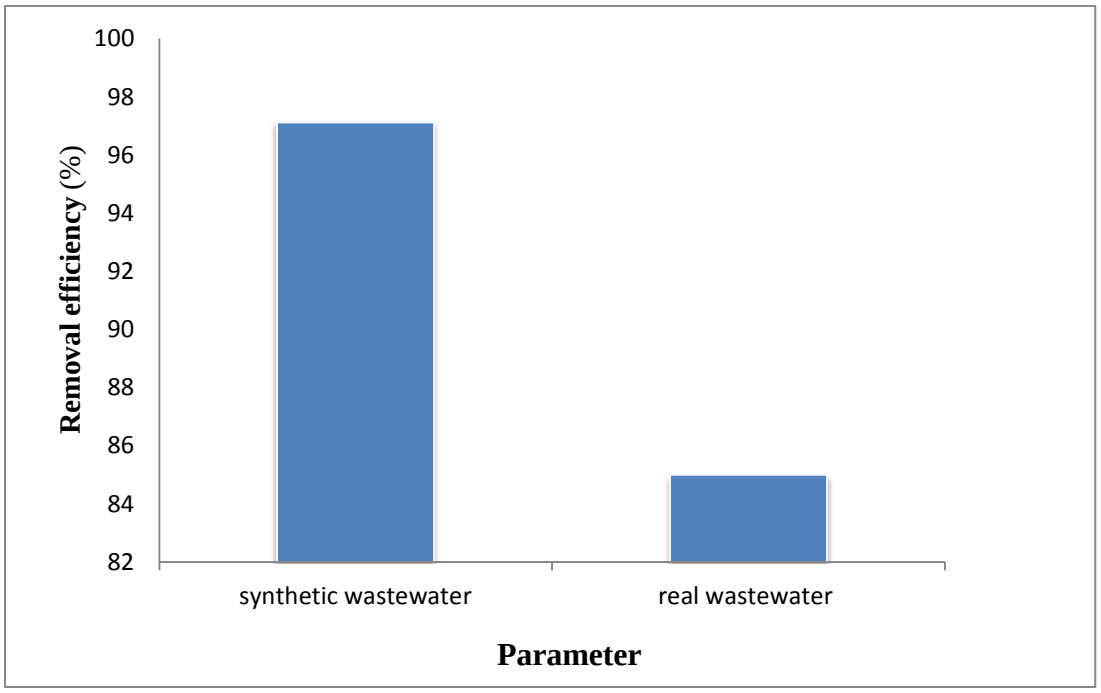


Figure 23: Removal efficiency of Pb (II) from real wastewater and synthetic wastewater.

Figure 24 shows that the removal efficiency of turbidity, COD, BOD_5, Cu (II), TSS and TDS from paint wastewater by using canna indica Linn stem activated carbon based on the lead removal efficiency optimal condition. In this optimal condition removal were obtained as 99.60%for turbidity, 93.65% for COD, 91.35% for Cu (II), 85.30% for BOD_5, 77.70% for TSS and 68.40% for TDS and 99.60 NUT for turbidity. In this study, it was observed that a high reduction of turbidity content of the paint effluent was obtained for the canna indica adsorbent used. This indicates that the canna indica activated carbon was an excellent adsorbent for turbidity reduction from paint effluent.

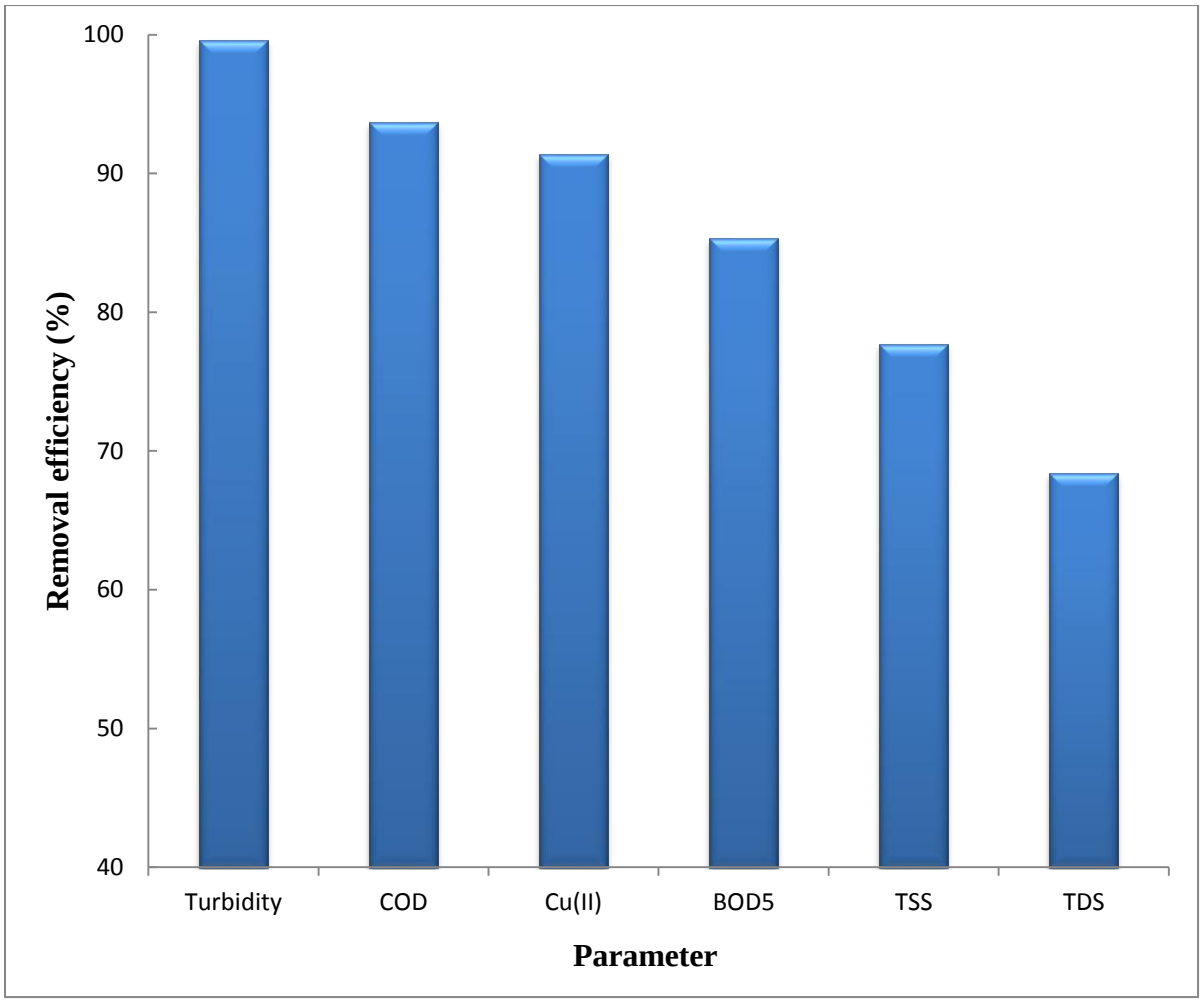


Figure 24: Removal Efficiency of Some Parameter.

4.9. Scale up Experimental Design of Canna Indica Stem Activated Carbon Production

pH =5

Mixing speed =200 rpm

Contact time =2hrs

Adsorbent dose =1.5gram

Raw waste water data from Nefas silk paint industry

2000 L wastewater discharged per day

Material balance

Assuming 300 working day in the year

2000 L = 1 day

X = 300day/yr.

Annual discharging of wastewater from Nefas silk paint industry

X= 2000L/day *300day/yr. =600,000L/yr. of wastewater discharge

Annual adsorbent dose requirement

1.5 gram =100ml

X =600,000

X = (1.5 gm *600,000L/yr.)/0.1L = 9,000 kg/yr. of canna indica activated carbon required

5. CONCLUSIONS AND RECOMMENDATION

5.1. Conclusion

Based on the result obtained within the frame work of this study it appears that the activated carbon prepared from canna indica Linn stem constitutes a good adsorbent for removing of pollutants from paint industry wastewater. The main conclusions that can be drawn from current study are given below:

- The physico- chemical analysis of canna indica Linn stem activated carbon results were found as *62.90 %* fixed carbon, *5.43%* moisture, *5.00%* ash, *26.67* %volatile matter, porosity *93.00%, 797.48* mg/g iodine number, specific gravity *1.51* g/cc and *0.44*g/cc bulky density.
- The initial wastewater characterization results were obtained as 2.95 for Pb (II), 1.95 for Cu (II), 171.00 for BOD_5, 2401.70 for COD, 619 .00 for TSS, 557.00 for TDS mg/L and 2791.33NUT for turbidity.
- The optimum conditions of Pb (II) removal from synthetic wastewater on the activated carbon were obtained as pH 5, adsorbent dose 1.5 and initial concentration 70 mg/L.
- According to the study results of adsorption isotherm showed that, the Langmuir isotherm model provides the best correlation of (R^2) was found to be 0.988.
- In the optimum conditions the removal efficiency of lead from synthetic wastewater and real wastewater were *97.12* and *85.3 %* respectively.
- The removal performance of Cu (II), BOD_5, COD, TSS, TDS and turbidity from paint wastewater at optimal condition were found to be *91.30, 85.30, 93.65, 77.70, 64.4*0 and *99.60%* respectively.
- Generally this study showed that, the adsorption process using canna indica Linn stem activated carbon were inexpensive, environmental friendly and effective adsorbents for the treatment of paint industry wastewater.

5.2. Recommendation

The following recommendations were made for the further study in the production and application of activated carbon from canna indica plant stem for the removal of pollutants from paint industry wastewater.

- In this study the adsorbent was modified by using phosphoric acid in order to increase negative surface charge of the adsorbent, so further researches should be investigated by using different types of acid and base to found high removal efficiency.
- In this study the activated carbon production from canna indica Linn plant stem was conducted with constant impregnation ration, carbonization temperature and ignition time to increase the yield of the activated carbon, therefore it is recommended further study by using different impregnation ration, carbonization temperature and ignition time to found maximum yield.
- For future research, it is recommended batch kinetic studies at various temperatures and agitation speed may be conducted to determine thermodynamic parameter for lead adsorption on canna indica Linn stem activated carbon as they were kept constant in this work.
- This research was conducted only the removals of the two metals (Pb and Cu) from paint wastewater, further work should be conducted on removal of other heavy metals by using canna indica linn stem activated carbon.

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Appendices

Appendix 1: List of material and instrument table

Instruments	Used to
Magnetic stirrer	Mixed sample
Rotary orbital shaker	Shacked sample
PH meter	Measured pH
Balance	Weighted sample
Furnace	Determined ash, volatile matter and TDS contents
Desiccator	Cooled the sample
Oven	Dried the sample
Attrition mill	Size reduction
Sieve	sieve analysis
Digital reading pipette	Taken the sample in a small scale
Volumetric plastic flask	Measured the volume
Sample bottles	Washed the material
Erlenmeyer flask 1000 litter	Prepared the standard solution
Turibido meter	Determined turbidity
Do meter	Determined turbidity
Thermometer	Measured temperature
Spectrophotometer	Determined COD
Bod incubator	Determined BOD_5
Atomic absorption spectrometer	Determined heavy metals (pb^{+2} and Cu^{+2})
FTIR	Determined the functional group
X- RD	Identified the sate

Appendix 2: list of chemical and materials

1. Phosphoric acid
2. Hydrochloric acid
3. Sodium hydroxide
4. Potassium iodide
5. Sodium thiosulphate grade
6. Lead nitrate, standard commercial grade
7. Indicator
8. Activated carbon
9. Filter paper
10. Iodine
11. Potassium nitrate
12. Acetylene, standard commercial
13. De-ionized distilled water

Appendix: 3 correction factor for iodine adsorption (B600-78- AWWA standard for activated carbon).

filtrate Normality	0.0000	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.000
0.0080	1.1625	1.1613	1.1600	1.1575	1.1550	1.1533	1.1513	1.1500	1.1475	1.146
0.0090	1.1438	1.1425	1.1400	1.1375	1.1363	1.1350	1.1325	1.1300	1.1288	1.127
0.0100	1.1250	1.1238	1.1225	1.1213	1.1200	1.1175	1.1163	1.1150	1.1138	1.111
0.0110	1.1100	1.1088	1.1075	1.1063	1.1038	1.1025	1.1000	1.0988	1.0975	1.096
0.0120	1.0950	1.0938	1.0925	1.0900	1.0888	1.0875	1.0863	1.0850	1.0838	1.082
0.0130	1.0800	1.0788	1.0775	1.0763	1.0750	1.0738	1.0725	1.0713	1.0700	1.068
0.0140	1.0675	1.0663	1.0650	1.0625	1.0613	1.0600	1.0583	1.0575	1.0563	1.055
0.0150	1.0538	1.0525	1.0513	1.0500	1.0488	1.0475	1.0463	1.0450	1.0438	1.042
0.0160	1.0413	1.0400	1.0388	1.0375	1.0375	1.0363	1.0350	1.0333	1.0325	1.031
0.0170	1.0300	1.0288	1.0275	1.0263	1.0250	1.0245	1.0238	1.0225	1.0208	1.020
0.0180	1.0200	1.0188	1.0175	1.0163	1.0150	1.0144	1.0138	1.0125	1.0125	1.011
0.0190	1.0100	1.0088	1.0075	1.0075	1.0063	1.0050	1.0050	1.0038	1.0025	1.002
0.0200	1.0013	1.0000	1.0000	0.9988	0.9975	0.9975	0.9963	0.9950	0.9950	0.9938
0.0210	0.9938	0.9925	0.9925	0.9913	0.9900	0.9900	0.9888	0.9875	0.9875	0.9863
0.0220	0.9863	0.9850	0.9850	0.9838	0.9825	0.9825	0.9813	0.9813	0.9800	0.9788
0.0230	0.9788	0.9775	0.9775	0.9763	0.9763	0.9750	0.9750	0.9738	0.9738	0.9725
0.0240	0.9725	0.9708	0.9700	0.9700	0.9688	0.9688	0.9675	0.9675	0.9663	0.9663
0.0250	0.9650	0.9650	0.9638	0.9638	0.9625	0.9625	0.9613	0.9613	0.9606	0.9600
0.0260	0.9600	0.9588	0.9588	0.9575	0.9575	0.9563	0.9563	0.9550	0.9550	0.9538
0.0270	0.9538	0.9525	0.9525	0.9519	0.9513	0.9513	0.9506	0.9500	0.9500	0.9488
0.0280	0.9488	0.9475	0.9475	0.9463	0.9463	0.9463	0.9450	0.9450	0.9438	0.9438
0.0290	0.9425	0.9425	0.9425	0.9413	0.9413	0.9400	0.9400	0.9394	0.9388	0.9388
0.0300	0.9375	0.9375	0.9375	0.9363	0.9363	0.9363	0.9363	0.9350	0.9350	0.9346
0.0310	0.9333	0.9333	0.9325	0.9325	0.9325	0.9319	0.9313	0.9313	0.9300	0.9300
0.0320	0.9300	0.9294	0.9288	0.9288	0.9280	0.9275	0.9275	0.9275	0.9270	0.9270
0.0330	0.9263	0.9263	0.9257	0.9250	0.9250					

Appendix: 4 Point zero charge determination

pH_i	2	3	4	5	6	7	8	9	10
pH_f	3.05	3.13	4.03	5..08	5.84	5.54	5.67	6	6.5
ΔpH	0.05	0.13	0.03	-0.08	-0.84	-1.46	-2.33	-3	-3.5

pHpzc determination

Fig1: pH zero point charge determination

Appendix Table 5: Analysis of Variance

Appendix table 5.1: Response for Removal Efficiency of Pb (II)

ANOVA for Response Surface Quadratic Model
Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F value	Prob>
Model	1255.26	9	139.47	20.43	<0.0001
A	286.40	1	286.0	41.95	<0.0001
B	146.43	1	146.43	21.45	0.0001
C	259.84	1	259.84	38.06	<0.0001
A^2	456.89	1	456.89	66.92	<0.0001
B^2	0.37	1	0.37	0.055	0.8173
C^2	3.73	1	3.57	0.52	0.4771
AB	0.10	1	0.10	0.015	0.9044
AC	3.73	1	37.74	5.53	0.0281
BC	37.74	1	3.73	0.55	0.4676
Residual	150.19	22	6.83		
Lack of fit	150.18	17	8.83	2944.64	< 0.0001
Pure Error	0.015	5	3.000E-003		
Core Total	1405.45	31			

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, A^2, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant

Std. Dev.	2.61	R-Squared	0.8931
Mean	89.78	Adj R-Squared	0.8494
C.V.	2.91	Pred R-Squared	0.7161
PRESS	399.03	Adeq Precision	17.755

The "Pred R-Squared" of 0.7161 is in reasonable agreement with the "Adj R-Squared" of 0.8494. "Adeq Precision" measures the signal to noise ratio.

Factor	Coefficient Estimate	DF	**Standard** error	95%CI Low	95%CI High	VF
A	3.99	1	0.62	2.71	5.27	1.00
B	-2.85	1	0.62	-4.13	-1.58	1.00
C	3.80	1	0.62	2.52	5.08	1.00
A^2	-7.99	1	0.98	-10.02	-5.97	1.00
B^2	0.23	1	0.98	-1.80	2.25	1.00
C^2	-0.71	1	0.98	-2.73	1.32	1.00
AB	0.092	1	0.75	-1.47	1.66	1.00
AC	1.7	1	0.75	-2.12	1.01	1.00
BC	1.7	1	0.75	0.21	3.34	1.00

Appendix table 5.2: Response of adsorption capacity

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F value	Prob>F
Model	745.45	9	82.83	93.56	<0.0001
A	7.18	1	7.18	8.11	0.0093
B	150.42	1	150.42	169.91	<0.0001
C	509.44	1	59.44	575.43	<0.0001
A^2	14.87	1	0.87	16.80	0.0005
B^2	0.87	1	54.25	0.98	0.3334
C^2	54.25	1	0.030	61.27	<0.0001
AB	0.030	1	1.46	0.034	0.8556
AC	1.46	1	16.48	1.65	0.2124
BC	16.48	1	089	18.61	0.0003
Residual	19.48	22	0.89	0.56	0.8315
Lack of fit	12.76	17	0.75		
Pure Error	6.72	5	1.34		
Core Total	764.93	31			

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, A^2, C^2, BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Std. Dev.	0.94	R-Squared	0.9745
Mean	10.45	Adj R-Squared	0.9641
C.V.	9.00	Pred R-Squared	0.9438
PRESS	43.01	Adeq Precision	34.594

The "Pred R-Squared" of 0.9438 is in reasonable agreement with the "Adj R-Squared" of 0.9641."

	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VF
Factor	9.91	1	0.32	9.25	10.56	1.00
A-PH	0.63	1	0.22	0.17	1.09	1.00
B- conc.	2.89	1	0.22	2.43	3.35	1.00
C- Dose	-5.32	1	0.22	-5.78	-4.86	1.00
A^2	-1.44	1	0.3	-2.17	-0.71	1.00
B^2	-0.35	1	0.35	-1.08	0.38	1.00
C^2	2.75	1	0.35	2.02	3.48	1.00
AB	-0.050	1	0.27	-0.61	0.51	1.00
AC	-0.35	1	0.27	-0.91	0.21	1.00
BC	-1.17	1	0.27	-1.74	-0.61	1.00

Appendix 6: Initial characteristic of Nefas silk paint factory wastewater

Parameters	Trial: 1	Trial: 2	Trial: 3	Average
P^H	5.75	4	6.40	5.4
Temperature (oc)	22.2	19.5	20.1	20.4
Turbidity (NUT)	2886	2588	2900	2791.33
BOD5 (mg/L)	158	190	165	171
COD (m/L)	2400	2395	2410	2401.66
DO (mg/L)	0.20	0.09	0.25	0.18
TSS (mg/L)	558	696	630	628
TDS (mg/L)	542	620	570	577.33
Pb(II)	3.02	3.02	2.75	2.95
Cu(II)	1.95	2.15	1.95	1.95

Appendix: 7 untreated and treated wastewater

Figure untreated and treated wastewater

Appendix 8: Some of used material photograph during the study

fig: 1 hot plate

fig: 2 sample collector plastic bottle

Fig 3: DO meter

Fig 4: pH meter

Fig: 5: spectrophotometer

fig 6: BOD incubator

Fig 7: oven

Fig 8: furnace

Fig 9: turbidometer

fig 10: digital balance

fig 11: digital shaker